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DENTAL COMPOSITES REINFORCED WITH MICROPOROUS SINTERED GLASSFIBER NETWORKS

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The SEM pictures on the cover show:

- front, a sintered microporous glassfiber network of low density.
- back, a condensed composite where the resin has been removed by combustion. The polished surface shows fairly large solid sintered areas. The cracks are artifacts produced during heating.



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PREFACE

This thesis is based on the following papers, which will be referred to by their Roman numerals:

- I. Ehrnford, L. A method for reinforcing dental composite restorative materials. *Odontol. Revy* 1976. 27. 51-54.
- II. Ehrnford, L. Composite laminate veneers with a continuous inorganic phase comprising micro-porous sintered glassfiber networks. *Acta Odontol. Scand.*, accepted for publication.
- III. Ehrnford, L. Composite resins with a condensable inorganic phase. *J. Dent. Res.* 1981. 60. 1759-1766.
- IV. Ehrnford, L. Surface microstructure of composite resins after toothbrush-dentifrice abrasion. *Acta Odontol. Scand.*, accepted for publication.
- V. Ehrnford, L. Surface characteristics of composite resins comprising a porous reinforcing filler - an in vivo study. *Acta Odontol. Scand.*, accepted for publication.

TERMINOLOGY

Throughout this study the following abbreviations and definitions are used:

Conventional composite - restorative resin based on inorganic filler particles with diameters in the 0.7 to 100 μm range.

Microfilled composite - restorative resin where the inorganic filler particles have diameters in the 0.005-0.7 μm range.

SGN - Sintered Glassfiber Network.

SGN-composite - restorative resin comprising porous (open pore) filler particles sintered from ultrafine (0.7-4 μm) glassfibers.

The term "composite" refers to a three-dimensional combination of at least two chemically different materials with a distinct interface separating the components (Broutman & Krock 1967). Thereby, properties are obtained which could not be achieved by any of the components acting alone. Accordingly hard tooth tissues and bone are composites but in dentistry the term generally stands for man-made "composite restorative materials". In this field the use of the terms "composite resin" or "composite" distinguishes a combination of inorganic aggregates bonded together with organic polymers from cements and unreinforced direct filling resins (Bowen et al. 1972). If the inorganic component should act as a reinforcement and not merely as an inert filler it should be bonded to the organic component (Broutman & Krock 1967). According to ISO standard 4049 the inorganic component should constitute at least 50 % of the weight of the restorative resin to be classified as a composite.

INTRODUCTION

The goal-directed basic research in which dental composite direct filling materials were developed was initiated at U.S. National Bureau of Standards in 1956. The research which was conducted by R. L. Bowen, resulted within a few years in useful restorative materials (Bowen 1962, 1963, 1965 a & b). The early history of the development of composite resins has been reviewed by Bowen et al. (1972).

Composite resins currently comprise the majority of the filling materials used for anterior dental restorations. These materials have many desirable properties, however their overall performance indicates the need for improvement (Dulik et al. 1981, Ruyter 1982). Especially there is need for improvement if they should also be used for restorations on posterior occlusal surfaces (Rümann & Lutz 1980). Here the most serious drawback is an unsufficient resistance to wear, which after a period of clinical service, will result in loss of "anatomical form" (Phillips et al. 1973, Leinfelder et al. 1980, Leinfelder et al. 1982, Lutz & Moermann 1982).

Fairly detailed information regarding the formulation of the inorganic and organic components in contemporary composites is available in the literature, e.g. Asmussen (1975), Bowen (1979), Ruyter & Sjövik (1981), Schaefer (1981) and Vankerckhoven et al. (1981), so in the following these matters will be only briefly reviewed.

Conventional composite restorative resins are based on the principles given by Bowen (1962, 1963, 1965 a & b). In these resins inorganic reinforcing filler particles are dispersed in a curable liquid resin. The particles are "silane treated" (e.g. with γ -methacryloxypropyl-trimethoxy silane) to promote a bon-

ding to the polymer. In the liquid there are additives which cause the resin to solidify but also additives which stabilize it until its hardening is desired. An example of the latter component is monomethyl ether of hydroquinone. The former additives are either as in "autocure" ("two-paste") materials a "catalyst" (e.g. benzoyl peroxide) and a "co-catalyst" (e.g. N,N-dihydroxyethyl-p-toluidine) or some kind of "photoinitiator" (e.g. methyl ether of benzoin as "UV-activator") in "photocure" materials.

The monomeric ingredients of the liquid resin generally comprises 2,2-bis(p-(2'-hydroxy-3'-methacryloxypropoxy)phenylene)propane often called BIS-GMA (Bowen 1962, Bowen 1963) with 30% (wt.) or more of a low viscosity diluent, such as TEGDMA (triethylene glycol dimethacrylate) (Asmussen 1975, Ruyter & Sjövik 1981, Vankerckhoven et al. 1981). Fairly high amounts of diluent is needed to give a workable consistency to the powder-liquid resin mixture. In order to obtain a low overall shrinkage (Cowperthwaite et al. 1979) and thereby optimum marginal adaption (Brauer et al. 1981) and a low water sorption (Cowperthwaite et al. 1981), the diluent content should be as low as possible within the limits of clinically acceptable working properties. In addition, a low diluent content seems favorable in view of achieving a good color stability of the composite (Asmussen 1981).

The inorganic filler is usually made of quartz or "X-ray-opaque glass". "Radiopacity" is achieved by incorporation of elements, such as strontium or barium, which have a relatively high atomic weight. The glass may be of the following composition: SiO₂, 50; BaO, 33; B₂O₃, 9; and Al₂O₃, 8 wt % (Bowen & Cleek 1972). Pyrolytic silica, which is used in "microfilled" resins (Gross & Schaefer 1974, Michl & Wollwage 1974), consequently, will not make these

materials "radiopaque". Generally it is agreed that the filler-resin ratio should be as high as possible to reach optimum physical and mechanical properties. Increasing this ratio would e.g. be expected to result in a relative decrease in hardening shrinkage, coefficient of thermal expansion, and creep, and a relative increase in modulus of elasticity (Bowen 1963). In order to get a low amount of interparticle resin the distribution of particle sizes should be wide (Bowen 1964). The sizes of the particles, however, affects several other properties. Some of these are the composites' surface texture and optical properties, and the viscosity of the filler-liquid-resin mixture.

Wear of composites involves an exposure of the inorganic filler by loss of resin matrix. Subsequently filler particles are debonded and lost and new resin matrix exposed (Bowen & Chandler 1973, Eames et al. 1974, Lutz & Moermann 1982). Filler particles protruding above a worn matrix thereby give the surface an irregular appearance, characterized by the type of inorganic filler used (Kusy & Leinfelder 1977, O'Brien & Yee 1980, Schaefer 1981, Lutz & Moermann 1982). Such exposure of the filler may occur as the result of a short period of toothbrush-dentifrice abrasion alone (Eames et al. 1971, Asmussen 1979, Soltész et al. 1980). If the inorganic filler particles have diameters of approximately the same dimensions as the wavelength of visible light ($0.4-0.7 \mu\text{m}$), a high tendency for light scattering may give rise to unfavorable opacity (Bowen 1964). Particles less than this size do not make the composite rough and matt when exposed in the surface, but increase the viscosity of the resin strongly and, in addition, make it thixotropic (Michl & Wollwage 1974). Thereby the possibilities of obtaining a high filler-resin ratio are counteracted when a paste or puttylike consistency of the mixture is required.

The exact mechanism of the in vivo wear process remains largely undetermined. The general consensus is, however, that occlusal stresses caused by the food and direct contact with the opposing tooth, play important roles. Kusy & Leinfelder (1977) suggested that in conventional composite resins, thermo-mechanical fatigue generates fine cracks at points of localized stress concentration, created by the motion of teeth during mastication and by rapid changes in temperature. Mechanical fatigue as part of the wear process has also been suggested by Draughn (1979) and Asmussen & Jørgensen (1982). According to Leinfelder (1981) the filler particles will fall out of position due to microcracking of the surrounding resin matrix, after a sufficient amount of polymer has been lost. Hard ceramic particles which serve as stress risers may cause a degradation of the resin matrix across the occlusal surface, which results in a generalized loss of material (Leinfelder et al 1982). According to Jørgensen (1978) the generalised loss of material with exposure of the enamel walls of occlusal cavities clearly indicates that the abrasion is caused by food compressed and sliding between the surface of the restoration and the opposing cusp during the action of chewing. Ruyter & Svendsen (1978) suggest chemical degradation of the resin and Wu et al. (1982) chemical softening, to accelerate in vivo wear. According to Söderholm (1981,1982) water attacks the glass particles which may facilitate failure at the resin-filler interface. Bowen (1979) claims the "weakest link" in the structure to be the interfaces between filler particles and the polymer. According to Thompson et al. (1979) a significant role in the debonding process may be played by the internal stresses at the filler-resin interface, created during polymerization.

Basic considerations. - The basic assumption behind this study was that a resin impregnated porous glass filler would have the advantage of mechanically interlocking with the resin matrix. Furthermore, it was thought that such filler particles would, given an appropriate microstructure, wear into a relatively smooth surface. As a consequence it would be possible to employ larger particles and thereby to reduce the amount of interparticle resin. A further reduction of this resin would be achieved if, in addition, the formulation could be made condensable in a way reminiscent of dental amalgam. It was thought that a structure with mechanically bonded and closely packed particles would be favorable in view of wear resistance. A condensation technique would also be expected to make improvements possible regarding other - previously reviewed - properties related to the amount and formulation of the resin. In particular, a marked reduction in polymerization shrinkage was thought to be desirable.

In some applications the ideal reinforcement may be a continuous inorganic phase. This could be achieved by impregnating a single premolded block of a porous inorganic component with a monomer, which subsequently is polymerized. A potential field of application would be e.g. preformed laminate veneers. Such veneers made from unfilled acrylic resins are now used for the restoration of fractured, badly malformed or stained incisors and canines (Boyer & Chalkley 1982). These acrylic veneers are however difficult to give a durable bond to the enamel (Boyer & Chalkley 1982). Furthermore, the resistance to wear of unfilled resins is low. Probably such veneers may be severely abraded by toothbrush-dentifrice abrasion alone. Provided the surface smoothness after brushing remains acceptable, a reinforcement might consequently be of interest, especially if this also improves the prerequisites for a durable bonding to the tooth.

Summing up, it was considered of interest 1) to find a method of producing a glass with interconnected pores of microscopic dimensions, but where the microstructure after resin impregnation would not be expected to give rise to unfavorable scattering of light; 2) to elucidate some potential fields of application.

AIMS

The principal aims of the present study were briefly:

1. -to suggest, as reinforcement in composites, a porous glass comprising ultrafine glass-fibers sintered into a three-dimensional network and to device a method of manufacturing such glass.
2. -to investigate whether it is possible to produce composite laminate veneers with a continuous inorganic phase comprising the sintered network.
3. -to find a condensable composite formulation where resin impregnated filler particles could be condensed to close contact.
4. -to examine the surface microstructure of composite resins (experimental and commercial) after toothbrush-dentifrice abrasion to establish what structural characteristics favor smoothness and lustre and to develop a method to rank experimental formulations in view of these characteristics.
5. -to study, in experimental composites, the surface characteristics produced by various finishing procedures and to examine a possible coherence between inorganic structure and in vivo wear patterns.
6. -to define parameters in the formulation of SGN-based composites of probable significance for the properties of the restoration.

REVIEW OF INVESTIGATIONS

I. A METHOD FOR REINFORCING DENTAL COMPOSITE RESTORATIVE MATERIALS.

The aim of the study was to suggest a reinforcement for dental composites comprising small inorganic components united to a three-dimensional network and to devise a method to manufacture such a structure from ultrafine glassfibers.

Material and Method

Glassfibers (soda-lime glass) of ultrafine diameters ($<4\text{ }\mu\text{m}$) were sintered by subjecting a cottonlike raw material to a certain combination of heat and pressure (650°C and 4 kPa). The resulting porous glass was studied with scanning electron microscope (SEM).

Results

The sintering resulted in a microstructure which had interconnected pores and was built from fibers united to a three-dimensional network. The microstructure appeared favorable in respect of strength and stiffness. Only minor areas (diameter less than $20\text{ }\mu\text{m}$) of solid sintered glass appeared.

II. COMPOSITE LAMINATE VENEERS WITH A CONTINUOUS INORGANIC PHASE COMPRISING MICROPOROUS SINTERED GLASSFIBER NETWORKS.

The purpose of the present study was to investigate whether it was possible to make thin composite veneers with favorable surface characteristics and a high resistance to toothbrush-dentifrice abrasion, comprising single blocks of SGN.

Materials and Methods

Sheets of SGN were manufactured according to the method described in Paper III. Such sheets, of varying thickness and density, were molded by the use of a vacuum-pressure method at approximately the same temperature used for sintering. Then they were acid leached, washed, silane treated and impregnated with a BIS-GMA-based liquid resin containing a photoinitiator. Curing of the resin was initiated by UV-radiation and was performed under nitrogen protection. Resistance to toothbrush-dentifrice abrasion was measured on impregnated sheets (average density before impregnation 1.5 g/cm^3) with the same method as in Paper III. Heat-cured poly(methyl methacrylate) and specimens from the UV-cured BIS-GMA-based liquid resin served as controls. Abrasion was measured both for a commercial and a standard dentifrice formulation. The brushed surfaces were studied in optical and scanning electron microscope.

Results

The vacuum molding process resulted in a sheet that satisfactorily reproduced the mold surface. On impregnation with a TiO_2 containing liquid resin, an enamellike appearance was achieved. Impregnation could be monitored so that a thin layer of SGN was left unimpregnated. Toothbrush-dentifrice abrasion rate (Table II in Paper II) was approximately the same for the two dentifrice formulations. Compared with the controls, abrasion of the experimental veneers was low. The resulting surface was lustrous, due to light reflecting glass structures, which formed a characteristic pattern in the surface.

III. COMPOSITE RESINS WITH A CONDENSABLE INORGANIC PHASE

The aim of this investigation was to find an SGN-composite formulation, preferably with a large average particle size and a high viscosity liquid resin, and a condensing technique that would make it possible to obtain a material with a close contact between the individual porous particles.

Materials and Methods

Liquid resin. - BIS-GMA based liquid resins containing low amounts of diluent (TEGDMA), a photoinitiator (benzoin methylether) and a stabilizer (monomethylether of hydroquinone), were prepared. Colloidal silica was added in various amounts in order to obtain liquid resins of increased viscosity.

Porous particles. - With a technique similar to that used in Paper I SGN was made with low and high (40 and 56% glass by volume) average density of the sintered bulk (sheet) material. By the use of a somewhat increased sintering temperature ($685 \pm 5^\circ\text{C}$) and spacers between the press plates the appropriate amount of down material (fiber diameter $2 \pm 1 \mu\text{m}$) could be sintered into the desired density. The sheets were ground and the powder sifted through standard sieves. The fractions were designated according to the size of the mesh openings (in μm) of the sieve, where it was collected, plus the next larger size. One fraction of "coarse" (250/160), two "medium" fractions (160/100 and 100/71) and one fine (71/40) fraction were collected. The powders were treated with 1-M hydrochloric acid for 24 h before being washed and silane treated. Powders were mixed which contained various amounts of the different particle fractions (Table in Paper III).

Specimen preparation. - Liquid resin was added to the powder to give mixes of different consistencies (Table in Paper III). In "saturated" mixes resin, just sufficient to impregnate the particles, was added. The powder-resin mixtures were placed into cylindrical cavities (diameter 4 mm, depth 2 mm). When consistency permitted, the material was condensed with a circular amalgam condenser (diameter 1.8 mm). Portions giving a 1-1.5 mm thick layer of condensed material were inserted at a time. Each layer was cured by exposure to UV-radiation for 60-80 sec. The surface of the specimen was then polished and the surface pores stained with black stamp ink. Specimens to be etched were cut in the midplane and the exposed cross-section surface was polished and etched in hydrofluoric acid and rinsed in distilled water. Plano-parallel cross-sections, approximately 80 μ m thick, were prepared for microradiography.

Measuring procedure. - To assess the air bubble porosity, the center of the specimen surface was studied on photomicrographs (dias, final enlargement $\times$ 400). The specimens were, according to their porosity, ranked into three groups; P1 with lowest, P2 with intermediate and P3 with the highest porosity. Vickers' hardness was measured on one-week old specimens. Etched surfaces were studied microscopically and the presence and extent of interparticle zones noted. Microradiography was performed with 12 kV 35 mA, CuK radiation. The porous particles were examined with the SEM. Polishability was studied by the use of white rubber discs at low speed on surfaces which previously had been ground with aluminium oxide discs (medium to superfine grits).

Results

The Table in Paper III shows that a close contact between the individual particles was obtained when

the powder resin mixtures were "dry" enough to permit application of a packing pressure approximately equal to that used for condensing dental amalgam (15 MPa). Excess monomer then appeared on the surface. With the powders containing "fine" particles (composites 6-10), no interparticle zones were found in any of the different resin formulations used. For the composite containing "high density" particles (composite 10) the highest hardness and lowest porosity were achieved. Microradiographs showed a structure including big particles of approximately the original size. On polishing with rubber discs surface lustre was observed.

IV. SURFACE MICROSTRUCTURE OF COMPOSITE RESINS AFTER TOOTHBRUSH-DENTIFRICE ABRASION.

The aim of the present study was to examine the surface microstructure of composite resins after toothbrush-dentifrice abrasion to establish what structural characteristics favor smoothness and lustre and to develop a method to rank the experimental composites in view of these characteristics.

Materials and Methods

Specimens made from an SGN-composite, a conventional composite and a microfilled composite resin were mounted side by side by the use of an unfilled resin. The set of specimens was ground on carborundum paper and polished with corundum powder ($0.3\ \mu\text{m}$) to a surface which showed an even lustre. The specimens were then brushed for one hour in a toothbrush-dentifrice abrasion machine. Specimen height loss was recorded for five sets of specimens. The same areas of the brushed specimens were then studied on micrographs obtained with scanning electron and optical microscop-

pes.

Results

The surface of the microfilled composite was, except for frequent pores, comparatively smooth and lustrous. The abrasion rate was, however, significantly higher than for the conventional and experimental composites. In the SGN-composite lustre was produced mainly by discrete light reflecting areas which in the SEM was identified as the glass constituent. These glass areas were slightly elevated and had smooth and flat surfaces except for rounded-off peripheral zones. These zones were not reproduced as light areas in the incident light micrographs. A corresponding phenomenon was observed in the conventional composite but not in the microfilled composite.

V. SURFACE CHARACTERISTICS OF COMPOSITE RESINS COMPRISING A POROUS REINFORCING FILLER-AN IN VIVO STUDY.

The purpose of the present work was to study the surface characteristics produced by various finishing procedures and to examine a possible coherence between inorganic structure and in vivo wear patterns of some experimental composite formulations.

Materials and Methods

Restorations were placed in lower premolars (Class I and II) and upper incisors (Class IV) and studied in the SEM on replicas (positive) made immediately after finishing or after a period of clinical service. The composite formulation was, except for "average SGN density", the same as that in experiment 10 of Paper III.

Finished surfaces were studied on Class IV and II restorations (av. SGN density 1.4 g/cm^3) which had been treated with either discs, 12-fluted carbide finishing bur, regular diamond bur or finishing diamond bur. The restorations studied after wear were finished either with of discs, finishing bur or a finishing diamond. The restorations studied comprised particles from SGN-materials of varying densities ($1.0\text{--}1.5 \text{ g/cm}^3$). The time they had been in clinical service ranged from 7 months to 29 months.

Results

Smooth surfaces both on enamel and composites were obtained with discs and finishing diamonds. The roughest surfaces were produced by the regular diamond. The carbide bur produced a smooth enamel surface, but a composite surface somewhat rougher than the finishing diamond burs and the discs.

After 20 months of clinical wear a Class IV restoration (SGN 1.4 g/cm^3) appeared lustrous, and presented in the SEM a surface with a pattern of smooth areas and areas with fine irregularities. On the occlusal surfaces of the Class II restorations (after wear) there were also found regions which only showed fine irregularities. The smoothest areas appeared where the particle density was high. Gross irregularities caused by as exposed particles surrounded by crevices were also observed. Exposed particles had a rounded-off surface profile. Also the microstructure within the particle surface showed a smooth outline. There was no evidence of "plucking out" of the inorganic phase.

DISCUSSION

Paper I shows that it is possible to sinter porous glass from extremely fine glass-fibers. The use of such glass in the form of a particulate filler or in larger pieces for the reinforcement of dental composites was suggested. The use in large elements was applied in an investigation on laminate veneers (Paper II) and the particulate filler in the studies on restorative resins (Papers III, IV & V).

Laminate veneer

Severely discolored anterior teeth can be masked with acrylic laminates (Faunce & Myers 1976). Three types of laminates are used: (1) modified denture teeth, (2) pre-formed laminates, (3) custom laminates fabricated by molding resin against a model of the patients' teeth (Boyer & Chalkley 1982). Composites are used to cement the laminates to acid etched enamel (Boyer & Chalkley 1982). By the use of unfilled acrylic for the veneers the surface will remain smooth for a long time of clinical service. But acrylic resin has a low resistance to toothbrush-dentifrice abrasion and often the veneers, "fall off". The site of failure is then usually between the laminate and the composite (Boyer & Chalkley 1982). The reasons for the frequent losses of veneers are not fully understood. Probably there is a low strength between the composite resin and the acrylic laminate. It can also be assumed that high stresses are generated at the interface as a result of the mismatch in thermal and possibly also the mechanical properties between the enamel and the veneer. In Paper II it was shown to be possible to make laminate veneers which were reinforced by a continuous SGN. These had, in comparison with unfilled acrylic resin, a high resistance to toothbrush-dentifrice abrasion. After such abrasion a surface lustre persisted. The used method

involved a step where a thin layer of the SGN could be left unimpregnated. Such a layer may prove to be useful the bonding to an intermediate composite resin. It should be investigated whether this and the supposedly "more enamellike" mechanical and thermal properties of SGN-reinforced laminates will yield more clinically durable veneers.

Restorative resin

In Paper I the use of porous particles was suggested as a means to interlock the inorganic and organic phases but also to lower the amount of interparticle resin in composites. The reason behind this was that, provided that the microstructure is appropriate, it was assumed to be possible to incorporate larger porous (than non-porous) particles, i.e. to widen particle size distribution, without at the same time to give the composite an unacceptable surface roughness after wear. The basic assumption was then that porous particles could be produced which would wear into a smooth surface profile. This assumption was supported by the findings in Paper V where SGN - particles showed a rounded-off surface profile. In Paper III a step further in the reduction of interparticle binder was suggested in making the formulation "condensable". The condensing technique was shown, in addition to permitting a close contact between the individual particles, to have the advantage of making possible the use of fairly viscous (and tixotropic) resins containing colloidal silica and low amounts of diluent monomer.

Other porous fillers. - Other types of porous reinforcing fillers have also been suggested. These are particles with a porous surface layer (Bowen & Reed 1976 a, b) and particles with internal (closed) pores (Mabie & Menis 1978). In the latter type the pores make the glass filler more readily cut by finishing

instruments. In the first type, glass particles have two separate, interconnected and interpenetrating vitreous phases. One of these is dissolved with an acid solution leaving a surface zone with extremely small pores, which can be filled with BIS-GMA resin. The depth of the surface zone need only be a few hundred Å (Bowen 1979). The "core" of such particles will however, on finishing or wear of a restoration, be exposed in the surface. The "dissolvable" phase should then not be attacked by acids which appear e.g. in juices and bacterial plaque. With adequate corrosion resistance such "semiporous" particles will probably provide improved resin-filler bonding in conventional filler systems.

Monomer formulation and micrograined additives. - The degree of conversion of a resin may be reflected in its mechanical properties (Asmussen 1982 b, Ruyter & Öysaед 1982 a) and possibly also in its resistance to chemical degradation (Ruyter & Svendsen 1978). With photoinitiation the curing depth is limited (Ruyter & Öysaед 1982 b) but in view of remaining double bonds this type of initiation is an efficient method (Asmussen 1982 a). Some, although little, diluent monomer seems required in the BIS-GMA resin (in connection with photoinitiation) to increase the degree of polymerization, thereby the tensile strength (Ferracane et al. 1982). The diluent will, however, also affect the polymerization shrinkage (Cowperthwaite et al. 1979, Brauer et al. 1981) and, as a consequence, marginal adaption of conventional composites (Asmussen 1975, Brauer et al. 1981). The shrinkage may possibly, in addition, cause the buildup of internal stresses high enough to cause microcracks in the structure. Coupled with the fact that water can penetrate the resin matrix, there is a risk that internal stresses may also contribute to stress enhanced corrosion of the filler. In these respects the amount of diluent should consequently be as low

as possible and, as far as possible, the shrinkage compensated by an equal hygroscopic expansion. For the latter purpose the use of hydrophilic diluents may prove advantageous (Bowen 1981).

By the incorporation of a micrograined filler, as the silanized colloidal silica (Aerosil^R) used in Paper III, it is possible to increase the contents of inorganic constituents. When used in substantial amounts this type of additive might probably also increase the wear resistance of the resin matrix (Jørgensen 1978, Lutz & Moermann 1982). Opacity to X-rays is probably most efficiently achieved by an adequate glass formulation for the SGN. This will be discussed later. Additives which further contribute to radiopacity may however also prove useful. A significant contribution is unfortunately not achieved by the used colloidal silica. For this purpose submicron additives such as particles of bariumsulphate or zirkoniumdioxide (Walkowiak et al. 1980) or "radiopaque" glass, as e.g. described by Bowen & Cleek (1969 & 1972), should be considered. Radiopaque additives such as barium (Braden 1978) and bromium (Braden 1982) may also be integral parts of monomers which might be used as diluents for the BIS-GMA resin.

In condensable formulations a system with two liquid resins may be employed, one for impregnating the particles and one to be added just before condensation (Ehrnfors, unpublished results). The purpose of the latter resin is then to provide the slight "excess resin" probably needed to avoid significant inclusions of air. The added resin will spread in the interparticle areas but is intended finally to appear mainly on the surface of the condensed restoration. Added in this way the resin could be used, if desirable, as a vehicle for agents which will affect the mode of polymerization and the final structure of the polymerized system (at least) in the interparticle

areas. If the liquid resin within the SGN-particles has an extremely high viscosity due to e.g. a high load of admixed micrograined filler the purpose may also be to improve handling properties (condensability) and reduce porosity by employing an "added resin" of lower viscosity.

Particle density and size distribution. - The density of the SGN-particles, and occasionally also their size, affects the surface appearance after in vivo wear as was shown in Paper V. So, in optimizing the filler formulation in respect of wear resistance the effect on surface texture must be considered.

On the esthetically important buccal surfaces of front teeth it is probable that toothbrush-dentifrice abrasion plays an important role in the degradation of surface finish of conventional composites. In Paper IV it was shown by the use of SEM that after in vitro toothbrush-dentifrice abrasion the exposed glass surfaces were smooth. Solid sintered areas in addition remained, except at the periphery, rather flat and appeared lustrous. The findings were corroborated in Paper II by the appearance of the laminate veneers after abrasion. The solid sintered areas will probably also be lustrous clinically. Lustrous restoration surfaces were as a matter of fact found in the in vivo study (Paper V). Such a surface showed smooth areas similar to those observed in vitro. From the latter study it was also concluded that the smoothest surfaces were obtained with particles of higher densities. It remains however to be answered whether clinically large solid sintered areas (Fig. 1 & 2), within the particles, are required to give a lustrous surface, or alternatively, a surface that at least is easy to keep clean from plaque and surface staining matter.

As shown in Paper IV (and II) the flat areas appeared

in photomicrographs (incident light) which made possible a convenient method of ranking different composite formulations. By the use of this method condensable formulations were found (comprising particles from sintered bulk materials of varying densities) giving a high filler-resin ratio (80 % wt, including 4% colloidal silica) in the cured composite (Ehrnford, unpublished results).

Increasing the particle density until large solid sintered areas appear frequently, will affect the occlusal wear pattern and probably also the wear resistance of the composite. Increasing the final filler-resin ratio in this way might also affect the effective linear shrinkage, appearing as e.g. cervical gap formation in Class II restorations. Formulations (condensable or "putty-like") comprising particles of extremely high densities (with or without large solid sintered areas) are, however, not necessarily clinically desirable but should be put to a test.

Particle size distribution strongly affects the working properties. For good condensability it is favorable to include large particles, such as in the largest size fraction (250/160) used in Paper III. These are considerably larger than the particles used in conventional composite resins. This fact as well as the condensing technique might affect mechanical strength. However, specimens made of condensable formulations comprising particles from this size fraction showed compressive (200-250 MPa) and tensile ("diametral") strength (45-50 MPa) of the same size range as some commercial resins of conventional type (Ehrnford, unpublished results).

To reduce the amount of interparticle resin there should probably also be included large particles in "putty-like" formulations. Handling properties would,

however, in this case benefit from the use of a comparatively lower maximum particle size, e.g. 100 μm .

Close particle packing and glass-resin bonding. - By the condensing technique the particles could be brought to close contact while excess resin appeared on the surface where it could be removed. It could be assumed that during this process resin will also appear along the cavity walls and fill out spaces where there otherwise would have been voids. On condensation interlocking of the particles makes the composite rather rigid. Clinically this facilitates the establishment of hard contact points and molding the surface of Class II restorations. Handling is facilitated if the material is precondensed to a coherent mass (in the laboratory) from which portions of desirable size can be cut (Ehrnford, unpublished results).

The close packing of the particles is achieved by a certain degree of crushing during condensation. The significance of such crushing has yet to be established. The new glass surfaces produced during condensation will probably be bonded to the resin by graft polymerization (Wollwage 1981). Unreacted silane (gamma-methacryloxypropyltrimethoxysilane) may be added as diluent monomer (Bowen et al. 1982) which may contribute to glass-resin bonding (Pluddeman 1974). This should be studied along with the possibility to pretreat the glass by the use of an improved method described by Chen & Brauer (1982).

Glass formulation. - An ideal glass would have, among other desirable properties, a refractive index (to visible light) very close to that of the polymer matrix (Bowen & Cleek 1969). The refractive index of the polymeric matrix varies somewhat, depending on its chemical composition, extent of polymerization, water content and other factors (Bowen & Cleek 1972). Although lower than usually required ($n=1.55$) according to Bowen & Reed (1976 a), in combination with the experimental monomer formulations the index of the soda-lime-silica glass ($n=1.52$) seemed appropriate. The glass should however also have a high corrosion resistance, which is not the case with the used type of glass (Söderholm 1981). Moreover, the glass should have a high opacity to x-rays to make the restoration easy to distinguish from the surrounding tooth tissues. This would facilitate the detection of decalcified dentin and enamel and draw the attention to overhanging margins, voids, or other defects that may be present in the restoration. Candidate glass formulations which may prove suitable in the above-mentioned respects have previously been presented (K-90, K-431 and K-429) by Bowen & Reed (1976 a). Another mode of increasing the radiopacity of the SGN would be to admix with the fiber raw material particles with this property. During the sintering procedure these particles would be locked into the SGN. It could also be assumed that this technique could be used to incorporate extremely hard areas into the SGN particles. For this purpose spheroidal particles of e.g. aluminosilicate glass or quartz may prove useful. The admixing technique may also be a way of obtaining a high concentration of micrograined additives, such as colloidal silica, in the interstices of the SGN.

Wear resistance. - The findings in Paper V suggest that porous particles can be worn in situ, interlocked with the resin. The mechanism and rate of occlu-

sal wear may, however, be influenced by several of the parameters discussed above in connection with SGN-composites. The relative impact on wear resistance of each of these parameters can only be speculated about, until established by clinical experiments.

However, it would be reasonable to assume that the wear resistance of the polymerimpregnated filler particles will increase (at least within certain limits) with the SGN-density. Marked differences in wear resistance between different areas within a restoration surface should probably be avoided as the resulting roughness might cause unfavorably high frictional stresses during (occlusal) wear. In conventional composites, where the particles remain intact during the process of occlusal wear, microcracks in the resin matrix (and subsequent filler exfoliation) has been hypotized to occur due to such stresses (Leinfelder 1981). In SGN-composites a corresponding phenomenon would be counteracted if there are only small differences in density between the particles or within the separate particles along with a close particle packing. Possibly also great surface area for bonding (along with a strong and stable bond) might be beneficial in this respect.

Marginal gap formation. - Penetration of oral fluids, bacteria or decayed food into marginal gaps may cause postoperative sensitivity, marginal discoloration, pulpal inflammation, decreased retention of the restoration and formation of secondary caries (Going 1972, Going 1979). Gaps around central composite fillings are formed as a result of polymerization shrinkage (Asmussen & Jørgensen 1972). These can however often be inhibited if the material is bonded to a rather wide zone of acid etched enamel (Asmussen 1974, Öilo & Jørgensen 1977). Conventional Class II cavities have mostly too little enamel available in the cervical part to prevent such gaps by the use of acid etching technique. In such restorations, which

in addition are often very bulky, it is of particular importance that the polymerization shrinkage is low. In an in vitro study comparatively small cervical gaps appeared in such Class II cavities by the use of a condensable SGN-composite (Ehrnfors & Derand, unpublished results). This may be explained both by a low polymerization shrinkage of the used monomer and by the structural buildup with contiguous, interlocking particles as shown in Paper III.

To completely avoid gap formation and thereby leakage in Class II cavities restored with composite resins, it is necessary to have strong adhesive bond to the dentin. Such an adhesive bond may possibly be provided by a recently developed method (Bowen & Cobb 1982). For the establishment and permanency of such bonding it is probably essential that tensile (and shear) stresses at the tooth-restoration interface, be as low as possible. Such stresses will probably appear, not only as a consequence of the polymerization shrinkage, but also due to thermal fluctuations and the action of masticatory forces. The effect of thermal fluctuations would be minimized if the thermal expansion coefficient of the composite closely approximated those of the tooth structure. For this purpose a high filler load in the composite is favorable. With condensable SGN-composite formulations the highest loads are probably achievable if a micrograined filler is included in the resin.

To minimize stresses at the interface due to masticatory forces the restoration should have a high degree of form stability. For this purpose a high elastic modulus, a high elastic recovery rate and low creep would be desirable. With no "dentin bonding" creep and an insufficiently high elastic modulus and recovery rate might possibly give rise to permanent or transitory changes in gap width (Jørgensen et al. 1976, Gjerdet 1976, Kremers & Krohn 1978, Ruyter &

Öysaed 1982). Mechanical form stability has, however, also been assumed to be positively correlated to wear resistance (Lutz & Moermann 1982). This assumption has been reinforced by the fact that in some studies the size of Class II restorations has been found to be positively correlated with wear rate (Mettler et al 1978, Lutz & Moermann 1982). A high form stability may therefore be of interest both to minimize marginal leakage (with or without "dentin bonding") and to achieve a high wear resistance.

Concluding remarks. - Summing up, primarily it should be established whether condensable composite formulations based on SGN may offer advantages in respect of thermal and mechanical stability of form. It should also be investigated if it is possible with SGN filler particles, preferably made from glass of high radiopacity and chemical durability, in combination with resins containing low or high contents of colloidal silica, to obtain composites with high resistance to occlusal wear.

CONCLUSIONS

1. A porous glass with interconnected porosity could be produced by sintering of glass fibers, with diameters in the 1-3 μm range, into a three-dimensional network (I).

The pore volume of this was possible to vary within wide limits (II, III).

2. Composite laminate veneers with continuous and interpenetrating organic and inorganic phases were obtained from vacuum-molded and polymerimpregnated SGN. A thin surface layer of the SGN could, by the used impregnation technique, be left unimpregnated to make possible a mechanical interlocking with an intermediate (between tooth and veneer) resin. The veneers showed (compared to unfilled acrylic resin) a high resistance to wear in an in vitro toothbrush-dentifrice abrasion test. After such abrasion smooth and lustrous areas were produced by exposed glass (II).

3. From SGN it was possible to prepare resin impregnable particles which could be used in composite resins with conventional ("putty-like") consistency or with a condensable formulation. Condensable formulations were developed, comprising fairly large particles and high viscosity liquid resins, which could be condensed by a technique similar to that commonly used with dental amalgam. The condensation resulted in 1) a "body" with SGN-particles packed closely together and 2) a firm surface covered with a layer of "excess resin" (III).

Restorations made from condensable formulations may be given a high finish (III, IV).

4. Surface smoothness and lustre after in vitro brushing with an abrasive type of dentifrice was favored if large continuous areas of glass were expo-

sed in the surface (IV).

5. Occlusal wear may result in a surface with irregularities reflecting the structural buildup of the individual SGN-particles. Surface smoothness is favored by a fairly high density of the SGN and by a close packing of the filler particles. Condensed composites in buccal restorations may remain clinically smooth and lustrous over an extended period of time (V).

6. The SGN-particle density, size distribution and glass formulation were parameters considered of importance for the properties of the composite. The use of resins (for impregnation of SGN-particles) which have high average molecular weight and/or high loads of micrograined additives, such as colloidal silica will probably be advantageous.

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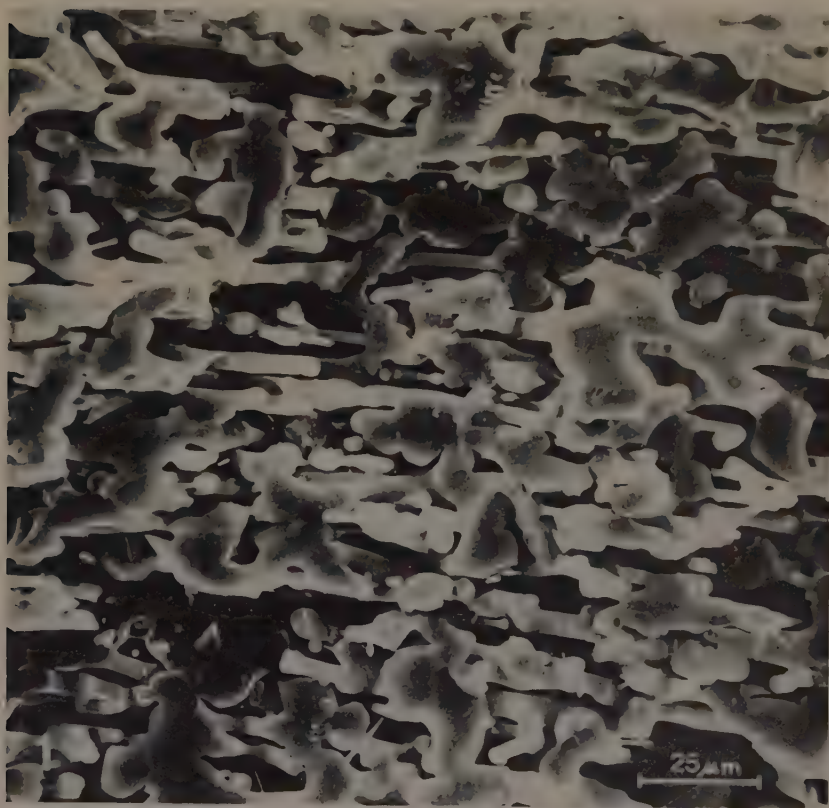
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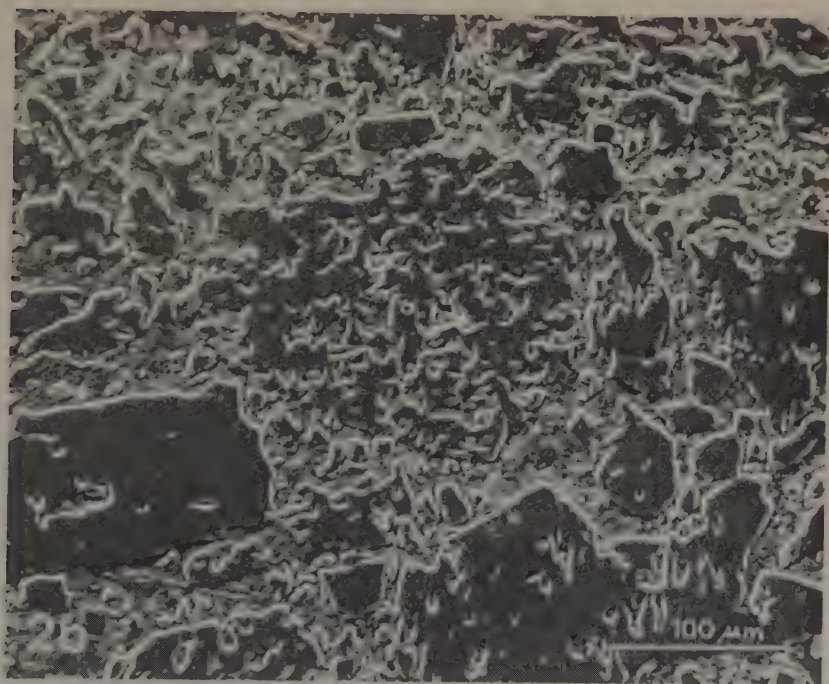
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Fig 1. SGN-sheet (unimpregnated) showing fairly small solid sintered areas in transverse fracture surface (SEM).

Fig 2. Condensed experimental composites with particles showing small (a) and large (b) solid sintered areas. Specimen surfaces first polished and then abraded with a highly abrasive tooth-paste (SEM).





Paper I

A method for reinforcing dental composite restorative materials

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Key words: Dental materials; composite resins

ABSTRACT

A method is presented for reinforcing dental composite restorative materials by incorporation of a polymer impregnated porous inorganic component. A method for producing such an inorganic component in the form of a three-dimensional glass fiber network is described. The structure of the network is demonstrated with the aid of scanning electron microscopy.

INTRODUCTION

Dental composite restorative materials should preferably resemble tooth substance in respect of appearance, mechanical strength, modulus of elasticity and resistance to wear. Other important properties of such materials are particularly those affecting the degree of microleakage, such as coefficient of thermal expansion, polymerization shrinkage and viscoelasticity.

It would therefore appear desirable that the resin part of a conventional composite material should be as small as possible. In addition, the bond between the inorganic filler and the resin matrix should be strong and stable.

Lack of an adequate bonding will, for example, permit dislodgement of filler particles from the surface of the restoration or ready penetration of water along the filler-matrix interfaces (Phillips 1973). Such inadequate bonding might be the main cause of the insufficient resistance of available composite resins to wear.

In an endeavour to obtain a high filler: resin ratio use is often made of filler particles with as wide a distribution of sizes as possible. But incorporation of large particles highly resistant to abrasion may be disadvantageous because of the consequent uneven wear and surface roughness of the restoration.

In the light of the above considerations it was therefore thought that an ideal dispersed phase would be a composite material consisting of polymer and small united inorganic components forming a three dimensional network. Since the polymer in the pores of such a network could be chemically bonded to the matrix polymer the retention of the inorganic component could be secured by mechanical interlocking.

The purpose of the present study was to find out whether it was possible to produce such an inorganic network of superfine glass fibres.

MATERIAL AND METHODS

The material consisted of superfine (diam. < 4 microns) glass fibres of A-glass type in a cottonlike form (supplied by Gullfiber AB, Billesholm, Sweden). This material was heated under pressure so that the fibers in contact were melted together to form a dense network. This network could be impregnated with a conventional type of BIS-GMA resin (EpoxyLite® HL — 72) with a vacuum method resembling the one described for the manufacture of a gypsum polymer composite (Ehrnford 1972).

For electron microscopy sheets, 250 microns thick, were prepared by compressing fiber material under pressure of 4000 Pa between two mica plates at a temperature of 650°C . During rotation the specimens were then coated in vacuum with a layer, about $200\text{\AA}$ thick, of a vaporized palladium-gold alloy (palladium 40 %, gold 60 %).

The appearance of the outer surfaces of a sheet as well as the fracture surface after it had been broken transversely was studied in the electron microscope (Cambridge Stereoscan Mark II:a). Photographs were obtained with Ilford Pan F film.

RESULTS

Fig. 1 illustrates that the individual fibres are united to form a continuous three dimensional network with microscopic pores. The structure and surface smoothness of the network is such as may be expected to give good mechanical strength and rigidity. Fig. 2 shows the appearance of the fracture region. The individual surfaces vary in size and shape, but most of them are less than 20 microns.

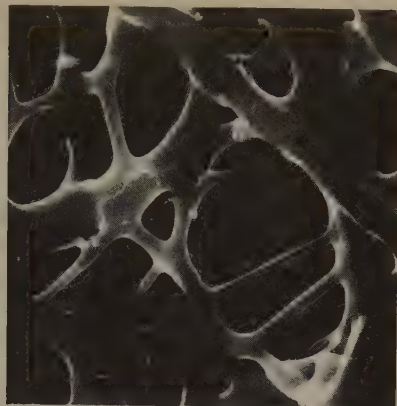
DISCUSSION

The electron microscopic study shows that the fibres had formed a three dimensional network. The interstices constituted a continuous system which made the material impregnable. Such impregnation could be performed with larger pieces of the material, which, after the impregnating material has hardened, for example, can be pulverized to a particulate filler. In this method the material used for the impregnation need not be identical with the matrix substance. Since also the chemical composition of the inorganic component as well as the density of the network can be varied, there are several possibilities of influencing the properties of such a filler.

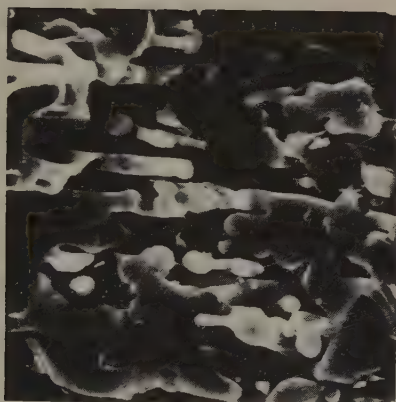
The inorganic network can be used not only in the manufacture of a particulate filler, but also in larger amounts for reinforcing dental restorations and for the construction of implants. These possibilities are the subjects of an investigation in progress.



1 a



1 b



2 a



2 b

Fig. 1. Fiber-glass network, surface a) $\times 600$ b) $\times 1200$

Fig. 2. Fiber-glass network, fracture surface a) $\times 600$ b) $\times 1200$

SAMMANFATTNING

En princip för förstärkning av dentala kompositer med en polymerimpregnerad porös oorganisk komponent anvisas. En framställningsteknik för en sådan oorganisk komponent, i form av ett tredimensionellt glasfibernätverk, beskrives. Nätverkets morfologi demonstreras med scanning-elektronmikroskopi.

Electronmicroscopic studies were performed at EM laboratory, Department of Zoology, University of Lund, Sweden.

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Paper II

Composite laminate veneers with a continuous inorganic phase comprising microporous sintered glassfiber networks.

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Composite laminate veneers with a continuous inorganic phase comprising microporous sintered glassfiber networks.

ABSTRACT

Veneers were made from sheets consisting of a three-dimensional network of sintered ultrafine glassfibers. The sheets were molded by a vacuum-pressure technique and then impregnated with a liquid resin. Impregnation was performed using a method which allowed depth of penetration to be monitored. The resin was cured with UV-radiation under N_2 protection. By the use of TiO_2 containing resins the veneer achieved an enamel-like appearance. An in vitro toothbrush-dentifrice abrasion test showed a high wear resistance and persisting surface lustre. Scanning electron and light microscopy showed fairly smooth and flat light-reflecting glass structures in the surface.

Key words: dental materials; composite resin; sintered glassfiber.

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Fractured, badly malformed or stained permanent incisors and canines are usually restored with crowns. Sometimes composite resin in combination with the acid etch technique is used when an alternative therapy is desirable. Composite resins have, however, their limitations in the difficulties to obtain a proper colormatching of adjacent teeth and in deterioration due to excessive wear and/or discolorations. Conventional composites often also demonstrate a rough surface after toothbrush-dentifrice abrasion (7). Another useful therapy is to use laminate veneers together with the acid etch technique (5). Modified denture teeth (6) or preformed laminate veneers (1), of unfilled resins, have been suggested for such veneers. The resistance to wear of unfilled resins is however low and these veneers may therefore be severely abraded by toothbrushing.

In a previous study reinforcement of resins with a sintered glassfiber network made from ultrafine fibers was suggested (2). Particles comprising such networks have later been used as the inorganic phase in a condensable composite restorative resin (3). This composite material showed a high resistance to in vitro toothbrush-dentifrice abrasion and compared to a conventional composite also favorable surface characteristics (4). Similar sintered networks may be used as a continuous inorganic phase for the reinforcement of laminate veneers.

The purpose of the present study was to investigate whether it was possible to make thin composite veneers, with favorable surface characteristics and high resistance to in vitro toothbrush-dentifrice abrasion, comprising single blocks of the sintered network.

MATERIALS AND METHODS

Production of veneers

Sheets of sintered three-dimensional glass-fiber networks were made according to a method described elsewhere (3). The sheets were then molded by means of a vacuum-pressure technique at approximately the same temperature previously used for the sintering.

The molds were made by means of a mastermodel comprising upper incisor denture teeth (Myerson Tooth Corporation, Cambridge, Mass. U.S.A.). These were mounted in acrylic resin in such a way that the facial surfaces protruded from a surrounding flat acrylic surface. A positive replica was made with a silicone impression material (Xantopren Blue^R, Bayer, Leverkusen, W. Germany) via a dental stone negative. In the facial surface of the positive replica approximately 30 stainless steel wires (diameter 0.25 mm, length 30 mm) were inserted, which later would form evacuation channels. To provide a channel for a thermocouple, a wire with approximately the same diameter was placed in the flat surface close to the replicated tooth. A final negative replica was now made by pouring an aluminous cement (Secar 250^R, Lafarge Aluminous Cement Co. Ltd. England) over the surface without covering the free ends of the wires. The cement was laterally bordered by a wax ring and thereby achieved the shape of a circular disc (diameter 65 mm). To avoid evaporation of water during setting, the free surface was covered with a plastic foil. After 24 hours at room temperature ($23 \pm 2^{\circ}\text{C}$) the wires were removed and the cement mold dried by slowly heating it from 100 to 400°C for 96 hours.

Impregnation of the molded sheets was performed with a liquid resin containing 75% wt. BIS-GMA (Freeman Chem. Corp. Port. Washington, Wi. U.S.A.), 24% wt triethyleneglycol dimetacrylate, a photo-initiator

(benzoin methyl ether 0.8%) and a stabilizer (hydroquinone-monomethyl ether 0.008%). In some experiments a pigment was also included (TiO_2 0.001%).

For the molding experiments sintered sheets of varying thickness and density were used. They were placed on the flat cement surface covering the concave mold. As much fine-grained quartz sand (art. 7536, Merck, Darmstadt, W.Germany) as could be hosted was then poured on top (Fig. 1). The cement disc was placed on a stainless steel tray provided with a thermocouple which reached contact with the sintered glass through the previously mentioned channel. The tray was then placed in a furnace with a temperature constantly held at 800°C , and was kept there until the temperature in the glass, after 15 minutes, reached 720°C . The disc was then transferred to a mouthpiece connected to a vacuum pump (Fig. 1b), which allowed a residual pressure of 0.1 atm to be momentarily established in the mouthpiece. The pressure was constant for 60 seconds. Due to the reservoir of hot air in the quartz sand the temperature, in spite of air leakage, was high enough for the few moments required for molding the sheets. Subsequent cooling by the air prohibited a further compaction of the sheet.

Before impregnation the molded sheet was treated with silane ("adhesion promoter") as previously described (3). Impregnation was performed in a vacuum mouthpiece comprising a beaker filled to the rim with glasspearls (diameter 1 mm). The sheet was placed on the glasspearls and covered with a thin polyester film which also covered the rim of the beaker. When air was evacuated from the bed of glasspearls the polyester film was firmly pressed into place and an opening could easily be cut to expose the veneer part of the sheet (Fig. 2a).

The opening was covered by the liquid resin which then was heated in situ by means of a jet of hot air ($65 \pm 5^{\circ}\text{C}$) to reduce viscosity, thereby promoting rapid impregnation. Evacuation was stopped when the sheet had achieved a translucency which made the glasspearls below completely visible (Fig. 2b). Curing was effected by exposing the sheet to UV-radiation (Nuva-Lite^R L.D.Caulk Company, Canada) for 60 seconds on each side. During this time the sheet was held in a stream of nitrogen to prohibit inhibition of polymerisation due to the presence of oxygen.

Abrasion test

Resistance to toothbrush-dentifrice abrasion was determined by the use of a method described elsewhere (4). The specimens were made from veneers with an average density of the sintered glass of 1.5 g/cm^3 . Heat-cured poly(methyl methacrylate) (Plexiglas^R, Röhm u. Haas, Darmstadt, W.Germany) and UV-cured unfilled resin specimens of the same monomer formulation as used for impregnation, served as controls. The specimens were ground flush with the holder on carborundum paper 600 and were subsequently polished on linen with an aqueous suspension of corundum powder (particle size designation $0.3 \mu\text{m}$).

After polishing, the specimens were brushed for one hour in 3 dl dentifrice slurry (paste to water ratio 1/3 by weight) by the use of a soft nylon toothbrush (TePe^R, Eklund & Pettersson AB, Malmö, Sweden). Brush load was 9 N, stroke length 20 mm and stroke rate 200 strokes per minute. At half of the total running time the specimen holder was rotated 180 degrees to reduce a tendency to channeling. On this occasion the slurry was also stirred to minimize sedimentation. In addition to the previously used commercial dentifrice (Sensodyne^R, Stafford-Miller Ltd. England) a standard dentifrice formulation was used. This consisted of 20% (wt) precipitated calcium carbonate (Fisher Scien-

tific Co., U.S.A.), 2% fluor of pumice (J. Mayer Co. U.S.A.), 2% methylcellulose (A4M, Dow Chemical Co. U.S.A.) and 75% deionised water. The resulting height loss was measured for 5 specimens of each kind. The brushed surfaces were studied in the light microscope with incident light. After coating in vacuum with an approximately 200-Å-thick layer of a palladium-gold alloy (palladium 40%, gold 60%), the same surfaces were studied with the scanning electron microscope (Cambridge Stereoscan Mark 11:a, Cambridge Instrument Co.Ltd. England).

RESULTS

The vacuum molding process resulted in a satisfactory adaption of the sheet to the mold surface. Coarse details in the surface were reproduced but not the openings of the evacuation channels. There was a reduction of sheet thickness especially for low initial sheet densities (Table 1). Impregnation with the liquid resin resulted in a fairly translucent material. On addition of TiO_2 pigment to the resin an enamel-like appearance was achieved. The veneers were also enamel-like in respect of brittleness which required careful handling on trimming by the use of rotating instruments. Partial impregnation was possible by regulating the supply of hot air. Thereby the impregnation process could be monitored and interrupted at a fairly well defined depth of penetration.

Toothbrush-dentifrice abrasion is given in Table 2. Abrasion rates of the same magnitude were found for both dentifrice slurries. In both cases the controls were abraded considerably more than the experimental veneer. By the use of the commercial paste, the poly(methyl methacrylate) wore at a rate approximately 17 times higher than the veneer. The surface after toothbrushing had a glossy appearance. Light reflecting parts as seen in the microscope were iden-

tified in the SEM as glass structures in a characteristic pattern (Fig.3).

DISCUSSION

The vacuum pressure method made it possible to mold sheets of sintered glass and thereby to predetermine thickness and density of the molded material. With subsequent polymer impregnation it was possible to leave a thin unimpregnated layer. Such a layer may, on bonding the veneer to the tooth, retain an intermediate layer of resin by mechanical interlocking. The molding and impregnation techniques were fairly simple and may well be practised in a dental laboratory with the necessary facilities.

In previous techniques for making veneers there seems to have been no way of combining a high resistance to toothbrush-dentifrice abrasion, as in regular composites, with surface smoothness and lustre, as in unfilled or "microfilled" resins. In dental composites the inorganic filler is dispersed in an organic, continuous phase. In resins with conventional filler-particles (1-100 μm) wear will expose particles in the surface, which then will be rough and dull. In the experimental composite veneer the structural buildup was different with continuous, interpenetrating and interlocking inorganic and organic phases.

The glass exposed in the surface gave the veneer a lustrous appearance. In a previous study (4) it was found that lustre was favored by the presence of large continuous areas of glass rather than the same amount of glass divided into smaller areas. The lustre therefore expectedly is dependent on molding parameters such as initial sheet density and molding temperature.

The toothbrush-dentifrice abrasion was low in compa-

rison with the heat cured poly(methyl methacrylate) and the UV-cured BIS-GMA based resin. The high wear resistance is therefore mainly ascribed to the inorganic network in the experimental veneer. The wear rate was of the same magnitude as previously found for a conventional and an experimental condensable composite resin (4).

Summing up, it was shown that enamel-like, preformed laminate veneers can be made in the form of a composite where the organic and inorganic phases are continuous and interpenetrating. These laminates had a high resistance to in vitro toothbrush-dentifrice abrasion and received a lustrous appearance after such wear.

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Table 1. Mean thickness of the sintered sheet before and after the molding procedure.

Sheet		Veneer
Density (g/cm ³)	Thickness (mm)	Thickness (mm)
0.3	2.0	1.0
0.3	1.0	0.5
0.3	0.35	0.15
0.5	2.0	1.2
0.5	1.0	0.7
0.5	0.35	0.22

Table 2. Toothbrush-dentifrice abrasion expressed as height loss in $\mu\text{m}/\text{h}$ (n=5).

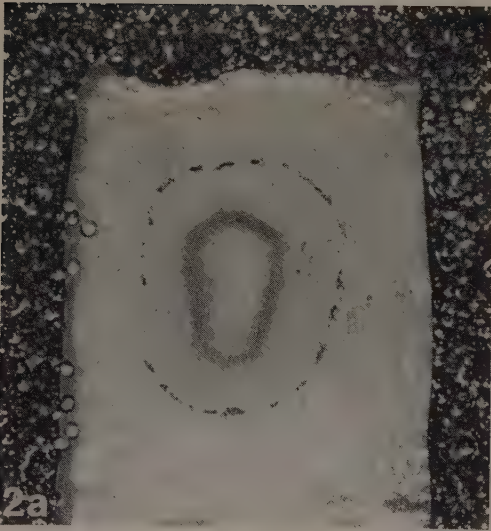
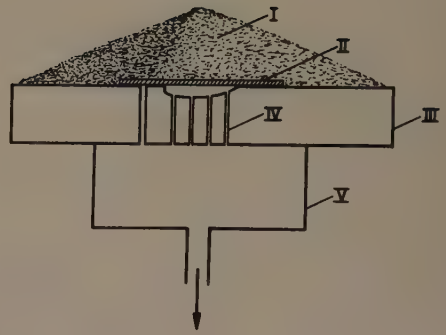
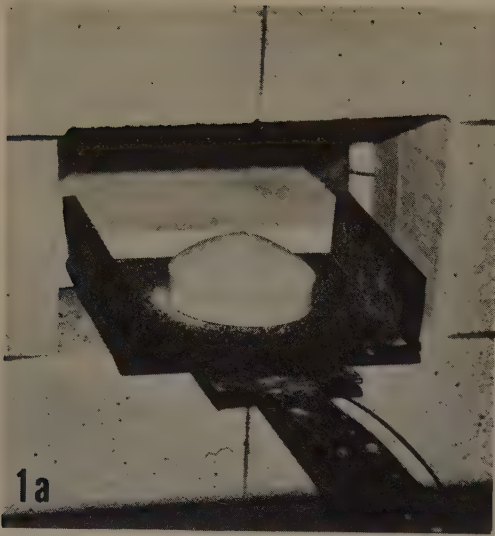
Material	Commercial paste		Standard paste	
	$\bar{X}$	$\pm\text{SD}$	$\bar{X}$	$\pm\text{SD}$
PMMA	76.7	14.1	77.3	4.3
Experimental resin	45.4	11.2	48.4	8.4
Experimental veneer	4.6	1.9	3.0	2.1

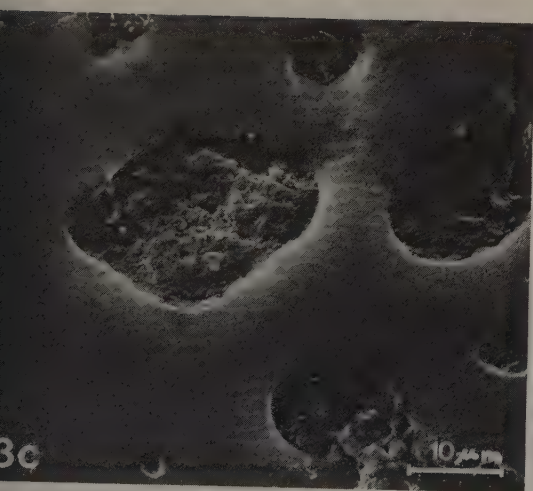
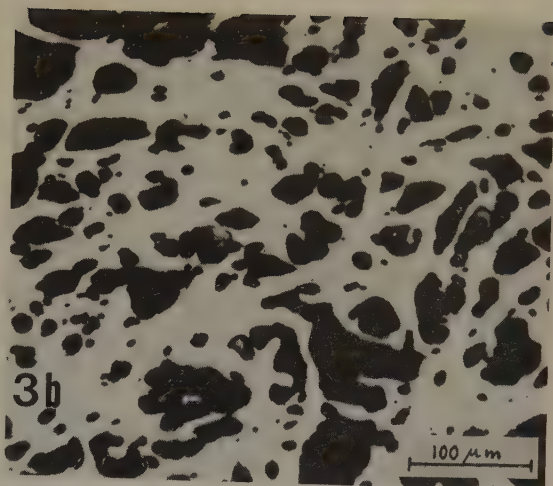
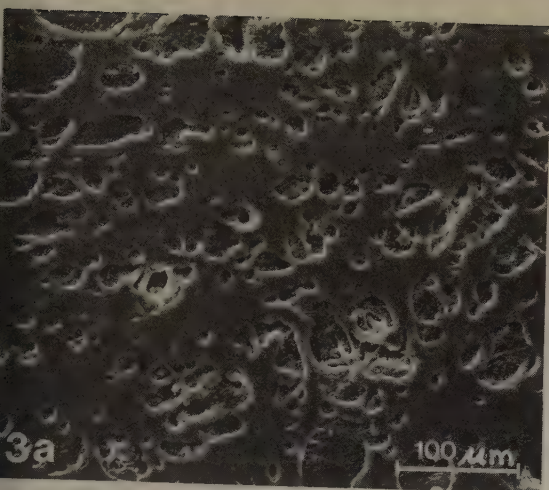
LEGENDS

Fig 1. Cement disc (mold) placed on tray provided with a thermocouple (a). The disc placed on a mouthpiece for evacuation (b); I quartz sand, II sintered sheet, III cement disc, IV evacuation channels, V mouthpiece connected to vacuum pump.

Fig 2. Molded sheet, partly covered by a polyester film, on a bed of glass pearls (a). After impregnation (polyester film removed) with liquid resin (b).

Fig 3. SEM (a and c) and light (b) micrographs showing the same surface area of a brushed experimental veneer. Part of a enlarged in c; note level and surface appearance of the resin.





Paper III

Composite Resins with a Condensable Inorganic Phase

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Open porous particles consisting of a sintered three-dimensional glass network were impregnated with BIS-GMA-based liquid resins. Formulations containing highly viscous resins allowed the particles to be condensed by a packing technique similar to that used for dental amalgam.

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Introduction.

A wide variety of reinforcing fillers have been used in composite resins. Early examples are fused silica particles and spherical glass fillers,^{1,3} as well as finely divided E-glass fibers and synthetic calcium phosphates.⁴ In more recent years crystalline quartz,⁵ barium-aluminoborosilicate,^{6,7} lithium-aluminosilicate crystalline compositions,⁴ pyrogenic silica,⁸ and other types of nonporous fillers have been introduced. A zirconium- and tin oxide-containing glass filler, with closed internal porosity for improved finishability, was reported by Mabie and Menis.⁹

To improve the bond between the filler and the polymeric binder, particles made of etchable glass with a porous surface have been proposed by Bowen.^{10,11} Another method has also been suggested to give interpenetration and physical interlocking of the organic and inorganic constituents; this is achieved by the use of a reinforcement consisting of a sintered three-dimensional network made from exceedingly fine glass fibers (< 4 μm diameter).¹² It was assumed that filler particles made from such a network could be incorporated in larger sizes than corresponding nonporous particles without impairing surface smoothness after wear. This would make it possible to use composites with a wider distribution of particle sizes and thereby to reduce the amount of interparticle binder.²

In the present study it was assumed that further reduction of the binder could be

achieved if, during the insertion procedure, the particles could be packed into close contact with excess monomer escaping through the network. Such condensation might make it possible to use very viscous liquid resins. Particles clinging together as a result of such condensation might also improve the handling properties of the unpolymerized material.

An acceptable putty consistency and the use of finer filler particles or higher filler concentrations in composite materials usually require the use of liquid resins of low viscosity. The inherently viscous nature of the commonly used bulky molecules, such as BIS-GMA,³ leads to the general use of a diluent, *i.e.*, a comonomer of a lower viscosity and molecular weight.^{4,13,14} Such lowering of the viscosity may be accompanied by an increase in shrinkage on polymerization and may also possibly increase the potential for tissue irritation.¹⁵ For the potential advantages of a high average molecular weight monomer and the possibility to increase the filler load with fractions of very fine particles, it was thought that the combination of high viscosity liquid resins and porous reinforcement fillers would be of special interest.

The aim of the present work was to find a composite formulation, preferably with a large average particle size and a high viscosity liquid resin, and a condensing technique that would make it possible to obtain a material with a close contact among the individual porous particles.

Materials and methods.

Liquid resin. — BIS-GMA† was diluted with TEGDMA (triethylene-glycol-dimethacrylate) in the proportions given in the Table. A photo-initiator (benzoin methyl ether 0.8%) and a stabilizer (monomethyl ether of hydroquinone, 0.008%) were

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†Freeman Chemical Co., Lot 124543, Port Washington, WI

added to the monomer composition. To get liquid resins of increased viscosity, colloidal silica^{††} was added in various amounts (Table).

Porous particles. — A technique similar to that described previously¹² was used for making the sintered glass-fiber network. A pair of square and planoparallel press plates (12 x 12 x 1.5 cm) were made of a hydraulic cement[§] in stainless steel molds. One of the flat press surfaces was provided with small projections (hemispheres) along the periphery to secure a minimum distance between the plates. The same plate was also provided with a thermocouple (Ni, Cr-Ni) with the measuring point centrally and partially exposed in the press surface. The temperature was recorded on a line recorder. To obtain even heating, the press plates were enclosed in a stainless steel box (wall thickness: 5 mm), just large enough to receive the two press plates. This technique made it possible to keep the temperature differences less than 10°C within the central area (65 x 65 mm) between the plates used for sintering. Fiber down[#] of A-glass type (soda lime) with a fiber diameter of $2 \pm 1 \mu\text{m}$ was used. It was placed between the plates and compressed by 3 kPa (the pressure produced by the total weight of the upper press plate and the upper part of the steel box). The loaded box was placed in an electric furnace which was automatically held at 800°C. When, after approximately 20 min, a temperature of $685 \pm 5^\circ\text{C}$ was reached in the measuring point, the sintering was stopped. The box was allowed to cool, and at approximately 300°C it was opened and the sintered sheet removed. Due to the spacers in the press plate, the sheet was then $775 \pm 25 \mu\text{m}$ thick.

The amount of glass-fiber down required between the plates to get the desired porosity was calculated with the use of a glass density of 2.5 g/cm^3 . Two degrees of porosity were used, one giving the sheet an average glass content of approximately 40% (low density) and the other approximately 56% (high density) by volume. The latter

corresponds to a volume percentage commonly found as the inorganic content of composites.

The sheets were crushed and ground with a porcelain mortar and pestle. The powder was sifted through a series of standard sieves (DIN 4188^φ), and the fractions were designated according to the size of the mesh openings (in microns) of the sieve where it was collected plus the next larger size. One fraction of "coarse" (250/160), two "medium" fractions (160/100 and 100-71), and one fine (71/40) fraction were collected. The powders were treated with 1-M hydrochloric acid for 24 h and then washed with distilled water and acetone.

A silane surface treatment of about 1/2% by weight of the powder was added as silane[¶] dissolved in acetone. The powder was allowed to dry at room temperature and was then heated at 110°C for 45 min. If, when gently compacted, the powder did not permit a droplet of distilled water to penetrate within five min, the silane treatment was considered satisfactory.

Specimen preparation. — The powder and liquid resins listed in the Table were mixed with the aid of a dental agate spatula on a glass slab. For "putty consistency," powder was added in a quantity large enough to make the mix as thick as possible (within the limits of workability). For "saturation," powder was added to the point where dry particles began to appear in the mixture, thus indicating the lack of excess monomer in amounts large enough for it to impregnate more particles.

The powder resin mixtures were placed into cylindrical cavities (diameter 4 mm, depth 2 mm) in acrylic rods (4 cm long) with a square cross-section (1 x 1 cm). When the consistency permitted pressure application, an amalgam condenser with a flat and circular condenser point (diameter 1.8 mm) was used. The force applied was measured by supporting the acrylic rod on a simple balance.

Condensation was performed at right angles to the cavity floor. It was started at the center, and the condenser point was then stepped over the surface until the latter was covered with overlapping marks. This

††Aerosil^R R-972, Degussa, Frankfurt, W. Germany

§Secar^R 250, Lafarge Aluminous Cement Co., Ltd., Essex, England

#Supplied by Bilsom AB, Billesholm, Sweden

φDeutsche Industrienormen

¶Silane A 174, Lot 803 080 174, Union Carbide Co.

was usually repeated; the first time a relatively low pressure was used to get a primary packing and a flat surface. When the maximum pressure (Table) was applied, it was kept constant for about one s. Portions giving a 1-1.5-mm-thick layer of condensed material were inserted at a time. Each layer was cured by exposure for 60-80 s to UV-radiation.^o

The cavities were overfilled with an excess of approximately 0.5 mm thickness to ensure complete removal of the oxygen-inhibited surface layer during finishing of the surface. Insertion and curing were done at room temperature ($22 \pm 1^\circ\text{C}$). The excess was removed and the specimen ground flush with the surface of the acrylic rod on carborundum paper No. 600. Subsequent polishing was then carried out on polishing linen with an aqueous suspension of corundum powder with a particle size designation of $0.3 \mu\text{m}$.

To assess air inclusion during the cavity filling procedure, the polished surface was stained with black stamp ink. When excess ink was wiped off, ink-filled pores could clearly be seen microscopically. Specimens to be etched were cut in the midplane, and the exposed cross-section surface was ground. The specimen was then mounted with cold-cure acrylic resin and polished as done previously. The surface showing a cross-section of the specimen was etched with hydrofluoric acid (40%) for $\frac{1}{2}$ h and rinsed in distilled water. Polished cross-sections were also prepared for microradiography. Using these planes as finished surfaces, planoparallel ground sections, approximately $80 \mu\text{m}$ thick, were then prepared with the technique described by Sundström.¹⁶

Measuring procedures. — To assess the air bubble porosity, the center of the specimen surface was photographed in a microscope (Vickers photoplan M41) using diafilm ($24 \times 36 \text{ mm}$, true enlargement $\times 50$). The picture was projected onto a frosted glass screen (final enlargement X400). The sum of the area of the pores with diameters ranging from 25 to $100 \mu\text{m}$ was calculated relative to the total area. Only pores larger than $100 \mu\text{m}$ were counted. This was done directly in the microscope (X40) and on the whole surface of the specimen ($12,56 \text{ mm}^2$). If two out of three specimens had

both less than 3% of the smaller sized pores and fewer than ten pores of the larger type in the total surface, the specimen was ranked as P_1 . If only one of these requirements was filled, it was ranked P_2 ; otherwise it was ranked P_3 . This method was shown in a preliminary study to be a convenient method for ranking some contemporary materials according to their porosity.

Hardness was measured on the polished surface of the specimen with a Vickers hardness tester^x and performed according to DIN 50133 with 10 kp load. Before being tested the specimens were stored for one wk ($22 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity).

Etched surfaces were studied microscopically in oblique incidental light (X40). When surrounded by resin with a low glass content, the large particles ($>40 \mu\text{m}$) were well defined. Notes were made of the presence and extent of such interparticle zones.

In each experiment one ground section was prepared for microradiography.[¶] This was performed with 12 kV 35 mA, CuK-radiation.

The appearance of the porous particles was studied with scanning electron microscopy.⁺ For this purpose particles were coated in vacuum with an approximately 200-Å-thick layer of a vaporized palladium-gold alloy (palladium 40%, gold 60%). For testing polishability, specimen surfaces were ground with aluminum oxide discs^{##} and then polished with a white rubber disc,^{oo} both at low speed.

Results.

The results of the investigation are presented in the Table. Fig. 1 illustrates the scanning microscopic appearance of a porous particle. Figs. 2 and 3 show the microradiographic and etched surface appearance of cured composites.

^xType Z3, 2A, Zwick & Co., Einsingen, üb Ulm/Donau, W. Germany

[¶]Phillips PW 1009, Phillips, Holland

⁺Cambridge Stereoscan Mark II:a, Cambridge Instrument Co., Ltd., Cambridge, England

^{##}Sof-Lex^R, medium, fine and superfine grits, 3M Co., St. Paul, MN

^{oo}Identoflex^R, type 1008, extra fine, Identoflex A.G., Buchs, Switzerland

^oNuva-Lite^R, L.D. Caulk Company, Canada

TABLE
APPEARANCE AFTER ETCHING, AIR-BUBBLE POROSITY, AND HARDNESS CHARACTERISTICS OF COMPOSITE
SPECIMENS CONTAINING POROUS PARTICLES OF VARYING SIZE DISTRIBUTION AND DENSITY

Composite No.	Composite formulation				Specimen characteristics			
	Porous particles		BIS-GMA liquid resin (wt%)	Colloidal silica in (wt %)	Mixture characteristics	Insertion method	Microscopic appearance after etching	Hardness (H _v 10) Mean ± S.D. (kp/mm ²)
	Type	Fractions						
1	Low density	Coarse (250/160, 70%) Medium (160/100, 20%) 100/71, 10%)	8	0	Putty consistency	Spatulation	Most particles surrounded by unbroken interparticle zones	P ₂ 131 9.7
2	—	—	8	0	Intermediate consistency	~ 5 MPa packing pressure	—	P ₂ 163 8.3
3	—	—	8	0	Saturated with powder	~ 15 MPa packing pressure	Particles in contact—only broken interparticle zones visible	P ₁ 211 12.1
4	—	—	8	11	Intermediate consistency	~ 5 MPa packing pressure	Most particles surrounded by unbroken interparticle zones	P ₃ 163 6.8
5	—	—	8	11	Saturated with powder	~ 15 MPa packing pressure	Particles in contact—only broken interparticle zones visible	P ₂ 209 9.6
6	—	Coarse (250/160, 70%) Fine (71/40, 30%)	8	11	—	—	No interparticle zones visible	P ₂ 232 7.6
7	—	—	8	19	—	—	—	P ₂ 244 15.1
8	—	—	20	19	—	—	—	P ₁ 247 4.6
9	—	Coarse (250/160, 52%) Medium (160/100, 26%) Fine (71/40, 22%)	8	11	—	—	—	P ₁ 249 16.7
10	High density	—	8	19	—	—	—	P ₁ 293 9.0

x: All values are from six measurements.

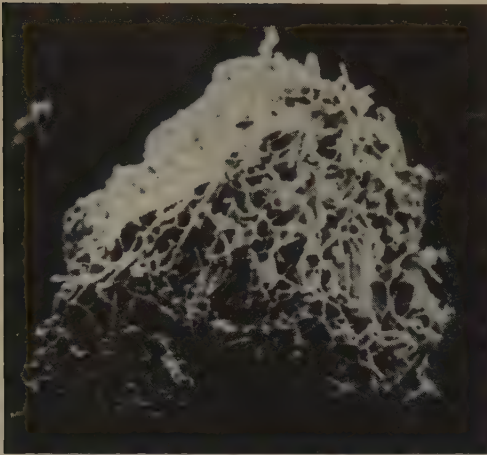


Fig. 1 — Open porous particle ("low-density"-type) consisting of a sintered three-dimensional glass-fiber network (265 X).

With "coarse" plus "medium"-sized particles (composites 1-5), a close contact between the individual particles and also the lowest value for air-bubble porosity was obtained using powder-resin mixtures "dry" enough

to permit application of a high packing pressure (15 MPa), the same magnitude commonly used for condensing dental amalgam.¹⁷ The same conditions appeared for resins containing both 0% and 11% colloidal silica. With the powders containing "fine" particles (composites 6-10), no interparticle zones were found in any of the different resin formulations used. Within this group the hardness number was of the same magnitude as that for composites containing "low density" particles (composites 6-9). For "high density" particles the hardness was higher (composite 10). In this experiment the composite also had the lowest air bubble porosity. In the three specimens the pore area percentage (pore diameters from 25 to 100 μm) was 1.7% or less, and the number of large pores (100-200 μm diameter) in the total surface area was four or less. Microradiography showed that the structure with no interparticle zones in the etched surface is mainly composed of the original large particles which have been crushed only to a minor degree.

With powder-saturated mixtures, the condensed material presented a firm surface

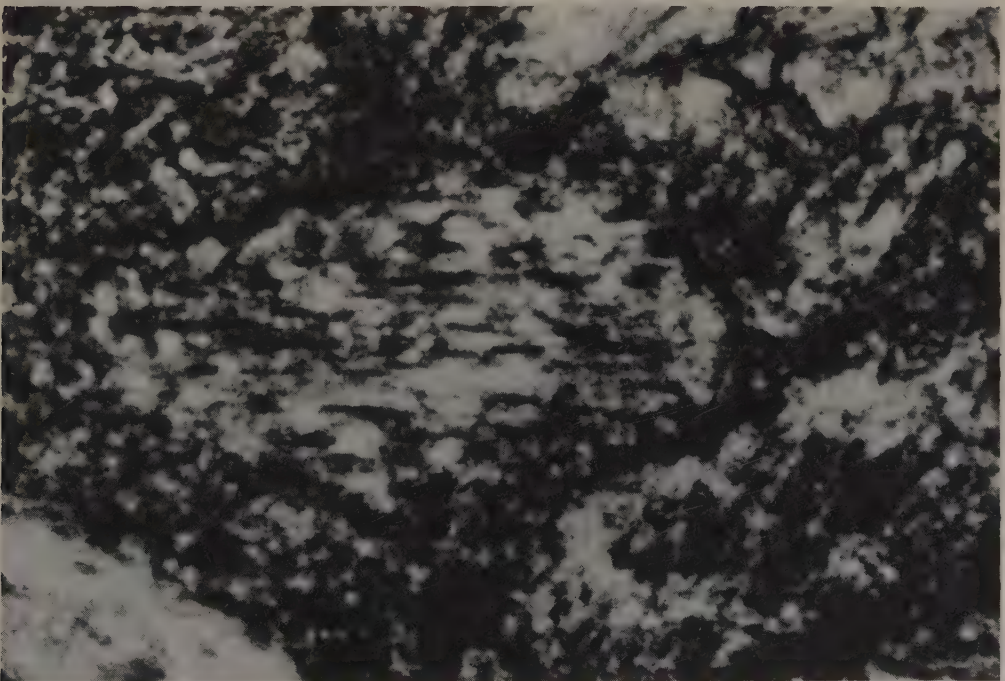


Fig. 2 — Microradiograph showing "low-density" particles in a condensed composite (390 X).

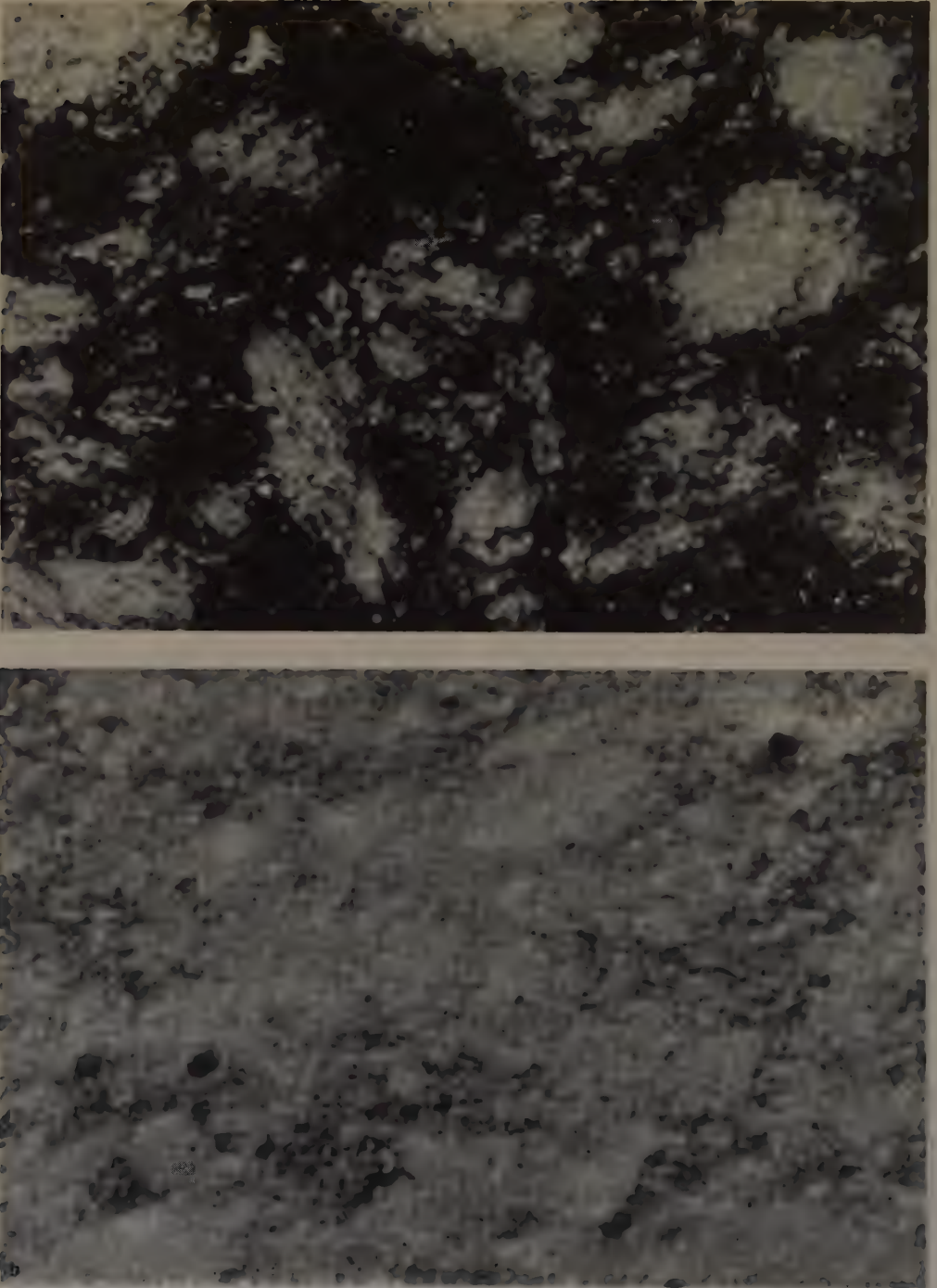


Fig 3 — Etched surfaces of composites containing "low-density particles": a) with low concentration of porous particles and b) when condensation technique has been used (140 X).

which could be molded with an amalgam condenser tip. When excess monomer appeared it was not more than just sufficient to give the surface a "wet" appearance. All the surfaces produced on polishing with rubber discs showed surface gloss which tended to increase with the hardness number.

Discussion.

The experiments with coarse plus medium-sized particles showed that it was possible to get both close contact between the individual particles and low porosity if the amount of excess monomer was small enough. If monomer is present in excess of what is necessary just to fill the networks, it will act as a lubricant between the particles. In too large amounts it will make the material flow under the condenser. With only a small excess, the particles could be brought to cling together and make the condensing process efficient. It is probable that during this process the particles are crushed to some extent in the area where they make contact. When the fraction of particles called "fine" was included, the crushing seemed to be sufficient to give a structure that appeared to consist entirely of closely packed particles without any inter-particle zones of high resin content. If required, silane treatment of surfaces produced by the crushing could probably be obtained by incorporation of silane into the monomer.

The Vickers hardness number of the polymers corresponding to the different liquid resin compositions differed, as shown in a preliminary study, only to a minor and negligible degree. The hardness number therefore mainly reflects the porous particle concentration and the density of the individual particles when other conditions, such as air-bubble porosity, are the same. For the different liquid resins used (composites 6-8), the particle concentration was roughly the same as reflected both in hardness number and microscopic appearance. Nor was there a change when a "medium" particle fraction was incorporated (composite 9). There was, however, a considerable hardness increase when "high density particles" were used (composite 10).

In all liquid resins, the amount of diluent was small compared with what is generally used.¹³ The condensing technique was feasible even when the viscosity was further

increased by incorporation of colloidal silica. This offers the choice of one or both of two possibilities: 1) the use of a monomer with a high average molecular weight, and 2) an increase in the inorganic component by incorporation of particles fine enough to penetrate the porous fiber network. For the latter purpose, particles of both colloidal and noncolloidal sizes, preferably of high radiopacity, could be considered.

Reduced shrinkage on polymerization can be achieved for BIS-GMA-based monomers which have high average molecular weight and high viscosity. An increase in average molecular weight results from reducing the amount or increasing the molecular size of diluent monomers or by incorporating molecules even larger than BIS-GMA. Decreased shrinkage during polymerization would result in less build-up of internal stresses¹⁸ and in reduced void formation. It is also possible that mechanical strength¹⁹ and color stability could be improved and the tendency for oxygen-inhibition of polymerization decreased by an increase in average molecular weight.

Variations in the density of the down-like raw material due to manufacturing and manipulation will affect the range of porosities of the individual particles. The electron microscopic observations of the particles, however, suggested that these variations were small. This may be partly explained by elimination of low-density areas in the sheet during grinding. As a consequence, the average glass volume in the particles may be somewhat larger than that in the sheet.

A high air bubble porosity decreases the strength of composite resins.^{20,21} Pores opening onto the surface will also retain plaque and staining matter. It is therefore important that the condensation technique seems to make a low air bubble porosity possible. Polishing of available composite resins with a rubber disc usually results in a dull surface due to exposure and "plucking out" of filler particles. The polish obtained with the porous particles is therefore probably related mainly to the mechanism of reinforcement retention, but is also affected by a number of variables, such as amount of interparticle binder, distribution of particle size, and particle porosity. Judging from the results, polishability is favored by a high particle con-

centration and a high density of the inorganic network. The optimum density of the network must, however, be determined on the basis of future studies on properties such as resistance to wear and mechanical strength.

Conclusions.

Reinforcing filler particles with open porosity can be prepared in three-dimensional networks made from extremely fine sintered glass fibers.

Such fillers can be impregnated with a monomer, used for a putty type of composite, or packed into close particle contact by the use of a condensation technique similar to that used with dental amalgam.

The condensation technique allows the use of high viscosity liquid resins and need not be accompanied by an increased amount of internal air voids.

Condensed composite resins can be made which have a high finishability after curing.

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Paper IV

Surface microstructure of composite resins after
toothbrush-dentifrice abrasion.

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Surface microstructure of composite resins after toothbrush-dentifrice abrasion.

ABSTRACT

In vitro, conventional, microfilled and experimental composite resin specimens were subjected to toothbrush-dentifrice abrasion. Subsequently height loss was recorded and the appearance of the abraded surfaces was studied in light and scanning electron microscopy. In the experimental composite, which had a polymer impregnated porous glass filler, the glass phase showed flat surfaces. These surfaces were more smooth and lustrous than the surrounding resin. They also showed a rounding-off in the periphery. In the experimental composite smoothness and lustre were therefore favored by the presence of large continuous areas of glass in the surface. It was possible to demonstrate the extension of the flat glass areas by the use of optical microscopy. In the conventional composite partly exposed irregular or rounded glass particles were frequent. A microfilled composite showed, except for frequent pores, a relatively smooth and lustrous surface. The wear rate of this material was, however, comparatively high.

Key words: dental materials; surface texture; porous filler.

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INTRODUCTION

A method for making composite restorations consisting of closely packed polymer-impregnated porous glass particles has been presented elsewhere (6). In this type of composite the inorganic and organic phases are mechanically bonded as they constitute interpenetrating networks. In optimizing the formulation in respect of inorganic network density and particle size distribution, properties related to the surface texture must be considered. Rough surfaces may lead to increased plaque retention and surface staining (10,14,15). Surface texture could also be of importance for the esthetical properties as it affects the reflection of light and the apparent shade of a translucent material. It is therefore desirable to obtain composite restorations with smooth surfaces which do not deteriorate in the course of time.

Composites containing conventional filler particles (1-100 μm) will after a couple of years often look dull, irrespective of their initial lustre (4,12). Surface roughness and loss of lustre may be caused by toothbrush-dentifrice abrasion alone (4,5,7,8,9, 11,13). On the esthetically important buccal surfaces of front teeth it is probable that such abrasion plays an important role in degradation of the surface finish. The appearance after toothbrush-dentifrice abrasion may therefore be one of the properties that should be considered when ranking different experimental composite formulations.

The purpose of the present study was to examine the microstructure of composites to find what structural characteristics favour surface smoothness and lustre. The aim was also to develop a simple method to rank the experimental composites in this respect.

MATERIALS AND METHODS

Formulation and manipulation of the experimental composite used was given previously (experiment No 10 in reference 6). For comparison one conventional (Profile,^x cat 057810 base 47812) and one "microfilled" composite (Silar,^{xx} cat 8A1, base 8A1) were used. The monomers in the composites were based on BIS-GMA resin.

The conventional and microfilled composites were mixed according to the manufacturers' instructions. The composites were then placed in individual cylindrical cavities (diameter 4 mm, depth 2 mm) in an acrylic rod with a square cross section (1x1x2 cm) at room temperature ($23 \pm 1^{\circ}\text{C}$). The commercial composites were covered with a polyester strip for a minimum of 5 minutes. The experimental composite was filled by the use of a condensation technique (packing pressure approx. 15 MPa) and cured by the use of UV-radiation as previously described (6).

Five specimens of each composite were made. After curing, the specimens were removed from the acrylic rod and mounted closely together in a row of three specimens, each of a kind, by the use of an unfilled acrylic resin (Sevriton Simplified^{xxx} Powder DD1, liquid TH) in a new acrylic rod which served as specimen holder. Mounting was performed in such a way that after the specimens had been ground flush with the holder, diametral planes of the specimens were exposed. Three specimens made from different composite resins, placed in random order, then formed an approximately 4 mm wide and 6 mm long row surrounded by a 2 mm wide frame of unfilled acrylic. For grin-

x S.S. White Co

xx 3M Dental Products Co

xxx De Trey Frères, S.A.

ing, carborundum paper 600 was used and subsequent polishing was carried out on polishing linen with an aqueous suspension of corundum powder with a particle size designation of 0.3 μm . Before testing, the specimens were stored for a minimum of seven days in air at room temperature and finally in deionised water for 23 hours at 37°C and one hour at room temperature.

Brushing was performed in a machine described by Björn & Lindhe (3). This gave a vertical back and forth movement of a soft nylon toothbrush (TePe^(R) Eklund & Petterson AB, Sweden) in a water dentifrice slurry of room temperature ($23 \pm 1^\circ\text{C}$). The slurry (3 dl) consisted of a dentifrice (Sensodyne^(R), Stafford-Miller Ltd. England), with a fairly high abrasivity index (16), and water in the ratio 1/3 by weight. Brush load was 8.7 N, stroke length 20 mm and stroke rate 200 strokes per minute. At half of the total running time the specimen holder was rotated 180° to reduce a tendency to channeling. On this occasion the slurry was also stirred to minimize sedimentation. The test was run for one hour which was well within the period under which the test showed proportionality between abrasion time and rate. A fresh slurry and toothbrush was used for every test.

Specimen height was recorded with a standard microcator for a central point on each restoration before and after each test. After the experimental procedure the specimens were first photomicrographed in incident light and then the same areas were studied with the scanning electron microscope (SEM).

RESULTS

When the experimental composite was studied in light microscopy, under low magnification (40 x) and incident light, it was observed that light was reflected mainly by discrete areas which formed a characteris-

tic pattern in the surface. The specimens which had been brushed, thereby achieved an uneven lustre also observable macroscopically. This was in contrast to the even lustre of the specimens which had only been polished. Fig. 1 (b) and Fig. 2 (a and b) shows details of the experimental composite surface in SEM and incident light. The pattern of discrete light-reflecting areas (Fig. 2 b) could be identified as corresponding to a pattern of comparatively smooth and flat elevated areas as seen in the SEM photomicrograph (Fig. 2 a). These elevations were produced by the glass constituent which was less worn and roughened by the toothbrush-dentifrice abrasion than the surrounding polymer. Comparison of the appearance in SEM and light microscopy also revealed that parts such as rounded-off peripheral zones of the glass structures were not reproduced as light areas in the light microscopy photomicrographs. Consequently, these gave an impression of a lower percentage of glass in the surface than was actually the case.

In the conventional composite, irregular areas in the surface were produced by the resin and partly exposed small particles (Fig. 2c). Most of these small particles appeared rounded-off. In incident light (Fig. 2d) the light-appearing parts correspond to flat surfaces on rather big particles as illustrated in the SEM micrograph (Fig. 2c).

The surface of the microfilled composite was, except for frequent pores, comparatively smooth (Fig. 1 a, b & c) and lustrous. The abrasion test showed a considerably higher abrasion rate for the microfilled than for the conventional and experimental composite resins (Table 1).

DISCUSSION

The surface texture of the conventional composite was

characterized by partly exposed irregular or rounded particles. On the largest particles flat surfaces with rounded-off borders could however also be seen. The loss of height on brushing was only a fraction (approximately 1/10) of the diameter of the largest particles. The flat surfaces were therefore most likely remnants of the original polished surface. Roughening of a conventional composite after only five minutes brushing by hand has previously been reported (2).

The surface appearance of the experimental composite indicated that the inorganic constituent was retained and that the abrasive action on the latter was less than on the polymer. The main part of the glass exposed in the surface, in contrary to the resin, presented a flat surface after abrasion which explains the uneven surface lustre observed macroscopically. Surface lustre therefore would be favored by an even higher glass/resin ratio than was used in the present experiment. A slight rounding-off of the peripheral parts of the glass surfaces indicates that light reflection may be enhanced by the presence of large continuous areas of sintered glass rather than small ones, the total percentage glass in the surface being the same. For the experimental composite, porosity was probably of no significance for the general surface appearance. In spite of a relatively high loss of substance a smoother and more lustrous surface appeared in the microfilled composite as a result of a more even wear of this material.

The rate of abrasion depends on several factors such as the type of dentifrice, the water/dentifrice ratio, the type of brush and the speed and pressure used during brushing (1,8,13). A study by Soltész et al (13) showed a significantly higher (up to 14 times) abrasion rate on microfilled than on conventional composites. Although there were differences in the

experimental procedure, this was in accordance with the presented results. It therefore seems as if the comparatively low loss of substance in the conventional and experimental composites is due mainly to the amount and type of inorganic reinforcement used in these materials and not to differences in the resin formulations.

In the experimental composite, except for the rounded-off borderlines, the light areas in the photomicrographs corresponded fairly well to the glass surfaces seen in SEM. With incident light angles kept constant and a standardized exposure and development procedure it should therefore be possible to rank experimental composite formulations, with reference to parameters related to the flat glass areas, on the basis of light microscopy photomicrographs. In such ranking it would be possible to utilize computerized image analysis.

Summing up, the method used seems suitable for ranking the experimental composites according to surface microstructure after toothbrush-dentifrice abrasion. Further, for these composites it could be concluded that the surface smoothness (and lustre) is favored by a high filler load and also by the presence of large areas of sintered glass. Clinically it is probably desirable that the surface is as smooth as possible. In optimizing composite formulation other properties of clinical importance must, however, also be considered. This will receive attention in a further study.

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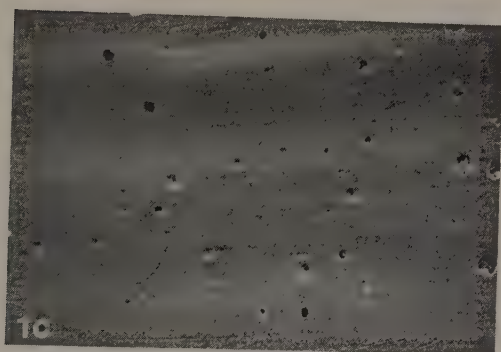
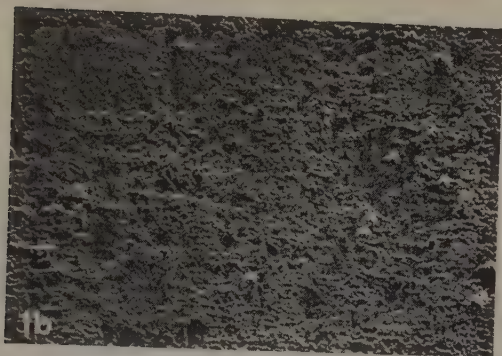
Table 1. Toothbrush-dentifrice abrasion expressed as average per hour height decrease $\mu\text{m/h}$.

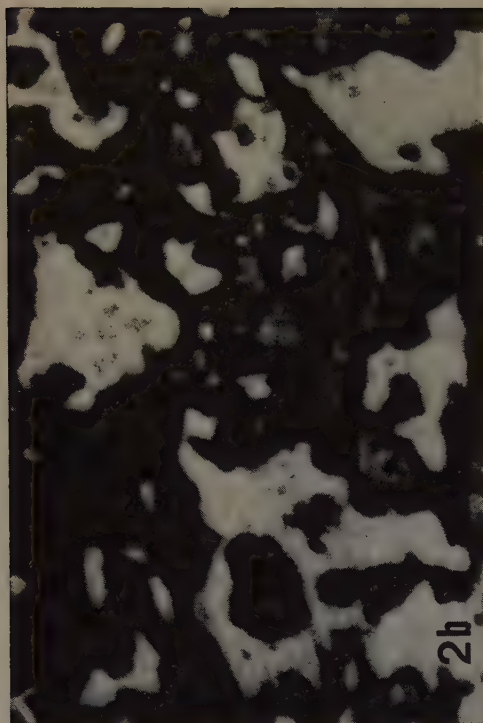
	$\bar{X}$	$\pm$ S. D.
Conventional composite	3.2	0.8
Unfilled resin	62.8	9.9
Microfilled composite	24.4	7.4
Experimental composite	2.2	0.8

LEGENDS

Fig. 1 Scanning electron micrographs showing brushed surfaces of composite resins with: conventional inorganic filler (a), experimental filler (b) and submicron inorganic filler (c).

Fig. 2 Scanning electron and light microscopy photographs of experimental composite resin (a and b) and resin with a conventional inorganic filler (c and d).





Paper V

SURFACE CHARACTERISTICS OF COMPOSITE RESINS
COMPRISING A POROUS REINFORCING FILLER - AN
IN VIVO STUDY.

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Surface characteristics of
composite resins comprising
a porous reinforcing filler
- an in vivo study.

Abstract

The surfaces of composite restorations with filler particles comprising an ultrafine sintered glassfiber network were examined in vivo. The effect of different finishing methods and clinical wear was studied with SEM on replicas. Smooth and lustrous buccal surfaces were obtained with finishing discs. On occlusal surfaces a microfine finishing diamond gave a good surface finish. After wear (> 7 mo) surface smoothness was favored by a close packing of the filler particles. The smoothest surfaces appeared when, in addition, the density of the sintered network was high.

Key words: dental materials; sintered network;
fiberglass; finishing; wear; surface microstructure.

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INTRODUCTION

A porous filler comprising a sintered ultrafine glassfiber network has previously been suggested for composite resins (4). In such composites the inorganic and organic phases constitute interpenetrating networks and are thus mechanically interlocked. The porous filler may be used in a conventional way dispersed in a liquid resin to a mixture with a putty-like consistency. In addition it is possible to use the filler particles in formulations where they may be condensed to close interparticle contact (5).

The average density of the particles may be varied within wide limits. In high density particles solid sintered areas appear within the network structure. In an in vitro study the presence of such areas favored surface lustre after toothbrush-dentifrice abrasion (6). It could therefore be assumed that after in vivo wear surface characteristics are influenced by both average density of the individual particles and by the amount of resin in between them.

In a study of early surface changes due to clinical wear the finished surface should be as smooth as possible. It is also essential to be able to recognise the surface characteristics produced by the finishing instruments. The purpose was therefore 1) to study the surface appearance after finishing and 2) to examine a possible coherence between inorganic structure and in vivo wear patterns of some experimental composite formulations.

MATERIALS AND METHODS

Composite resin restorations were placed in lower premolars and upper incisors. The patients were adults with intact or almost intact dentitions and with no crown and bridgework in contact with the teeth that should be restored. They all had good oral hygiene and brushed their teeth one to three times a day with conventional types of abrasive dentifrices. The used composite formulations were, except for the average density of the sintered glassfiber network (SGN), approximately the same as previously given (experiment no 10 in ref. 5). Finishing procedures were studied on Class II and Class IV restorations (average SGN density 1.4 g/cm^3) made by the use of a condensing technique (5) and a fairly high packing pressure (approximately 15 MPa). The finishing was made after approximately one week of clinical service. Surface characteristics after in vivo wear was studied on restorations where the materials had been inserted by the use of varying packing pressures. Buccal and occlusal surfaces were used to illustrate different surface appearances. These were selected from a total of 14 restorations (7-29 mo) from different patients. The presented surfaces belonged to restorations given in Table 1. For comparison a conventional composite was also included.

Finished surfaces were studied after use of the following instruments: discs (Sof-Lex)^R; grits 360, 600 and 1200; 3 M Dental Products, St. Paul, Minn. USA), finishing burs (Jet^R La 7006, 12 fluted carbide bur, Beavers Dental Prod. Ltd., Ontario, Canada) a regular round diamond bur (DB 106, AB Dentatus, Hägersten, Sweden) and a round microfine finishing diamond bur (ComposhapeSet^R, CSR 5400, W. Hubschmid & Sohn, Lugano, Switzerland). The instruments were used at low speed (2000-3000 rpm) and with water spray, except for the discs which were run dry. The finish-

ing diamond bur was also used at a high speed (100,000-200,000 rpm). The restorations studied after wear had been finished with the following instruments: Class IV - finishing disc; Class I and II - finishing bur or finishing diamond.

Clinically the surfaces were compared with the surface of a piece of enamel (Fig. 1), by the use of a sharp explorer. The enamel was cut from central part of a buccal surface of a premolar. Finishing and wear patterns were studied with the scanning electron microscope (SEM) on replicas made with a two-stage replication technique (7). Impressions were taken with a silicone impression paste (Xantopren Blue, Bayer Dental, Leverkusen, W. Germany). A primary impression was taken only to clean the surface. The second impression was cast with an epoxy resin (Orthobond,^R Vernon Benshoff Co, Inc., Albany, NY, U.S.A.). The positive replicas were coated, by cold sputtering, with approximately 200 Å of gold before being studied in the SEM (Cambridge Stereoscan Mark II:a).

RESULTS

The regular diamond bur produced a rough surface on both enamel and composite (Fig. 2a). This was the only finished surface which was ranked rougher than the test piece of enamel. The finishing diamond bur produced a fairly smooth surface with minor grooves of similar (and typical) appearance in enamel and composite (Fig. 2b). When used at high speed a gouging out of the surface appeared. The discs produced a smooth and lustrous surface in both enamel and composite (Fig. 2c). The carbide bur produced a smooth surface in the enamel but a composite surface that seemed somewhat more irregular than that obtained with the finishing diamond burs and the discs (Fig. 2d).

The Class IV restoration studied after wear 20 mo, clinically appeared lustrous and was on probing ranked equal to the enamel. In the SEM fine irregularities appeared alternating with smooth almost textureless areas (Fig. 3). The individual particles were not aligned by continuous crevice formations. In the Class II restorations (after wear) occlusal areas were found resembling the Class IV restoration but also areas which only showed fine irregularities (Fig. 4). In the restorations with a low average density of the sintered network (SGN 1.0 g/cm³) the appearance of these fine irregularities was fairly equal on the entire occlusal surface. In the restorations with the higher average SGN densities the surface texture was more varied. On one of the Class II restorations (2 years, SGN 1.0 g/cm³) a pronounced "hilly" appearance was observed comprising partly exposed particles surrounded by continuous crevices (Fig. 5). Exposed particles had a rounded-off profile and sometimes, as seen on the 7 months old Class II restoration (Fig. 6), showed a marked surface microstructure. In the SEM rather smooth areas were

observed when the network seemed dense. This is illustrated in Fig. 6 which shows an exposed particle with a solid sintered area and another area where the density of the network appears to be high and the surface microstructure rather smooth. There was also on the microstructure level a smooth outline with no signs of gross fractures or "plucking out" (Fig. 6). In Fig. 7 surface details from an experimental composite (a) and a control (b) on the same premolar are illustrated. In contrast to the experimental resin the control shows particles with sharp angles. A gap, which possibly may have been caused by filler dislodgement, can also be seen. The surface of the control was on probing ranked as rougher than the enamel test piece. The occlusal surfaces of the experimental restorations showed parts which were ranked as equal to the enamel, but also those which were rougher.

DISCUSSION

After finishing, the smoothest surfaces were obtained with the discs in accordance with previous findings (3,9). This smoothness may, however, to a certain extent be produced by surface smearing on both enamel (2) and composite (1). On composites such smearing is produced by the resin and the appearance of the surface may therefore change after a short period of toothbrush-dentifrice abrasion (1). The second best surface was obtained with the finishing diamond. This instrument has previously been shown to perform favorably in comparison with a number of other finishing methods (8). It therefore seems to be the instrument of choice for surfaces where the discs can not be used. The ground surface has the advantage of a characteristic appearance with small grooves which are easy to recognise in the replicas. In connection with gross excess, however, tungsten carbide burs may be preferable as the risk of severe damage to the enamel then seems low (9).

Buccal surfaces of front teeth should not only have a low surface roughness to make them easy to clean but generally it is also considered desirable for them to give an "enamel-like" lustre. In the Class IV restoration a major part of the surface was still smooth and lustrous after 20 months of clinical service. This was probably due to both the fact that the particles were closely packed and that the density of the individual particles was fairly high. The smooth and almost textureless areas in the replicas has an appearance closely resembling areas previously observed (in the SEM) on specimens subjected to in vitro toothbrush-dentifrice abrasion (6). They were then identified as lustrous areas of solid sintered glass. It is however also possible that in the restoration there were parts which were not sintered to a solid but where the density of the glass network was suffi-

ciently high to give a similar appearance.

On occlusal surfaces there is no need for surface lustre. Usually they are also easy to keep clean. To be comfortable to the patient the surface must however be such that it feels smooth to the tongue. The surface profile reflecting the individual particles should therefore be smooth with no marked crevice formation in between the particles. At this level the texture would be determined by both particle size distribution and the density to which the particles have been packed. The crevice formation illustrated in Fig. 5 thus indicates that the particles have been packed to an insufficient closeness. The surface of the individual particles seemed to increase in smoothness with increasing density of the glassfiber network. Apparently at least some of the restorations comprised particles representing a wide distribution of densities.

No signs of fresh fractures or of "plucking-out" were observed. Rather, the surface was characterised by its rounded microstructure which indicated that glass had been worn away without dislodgement of gross particles. Considering the risks for crack formation (due to mechanical stress) at glass-resin interfaces and within interparticle resin, it is probably favorable if filler particles are both smooth (rounded-off) and mechanically interlocked with the resin.

It could be concluded that clinically the experimental composites could be given a high finish. After a period of clinical wear fairly smooth surfaces appear where the density of the network seems high. The particles should preferably be closely packed. The use of particle size distributions including fairly big particles may prove useful to minimize the border areas and thereby the risk for crevice formation.

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Table 1. Restorations studied after wear

Class	Clinical service (mo)	Average SGN density (g/cm ³)
IV	20	1.4
II	12	1.4
II	24	1.0
II	7	1.5
I	29	1.0
I	29	†

† Adaptic^R (Batch 7F023, Johnson & Johnson Dental
Products Co, East Windsor, N.J. U.S.A.)

LEGENDS

Fig 1. Surface of enamel used as control.

Fig 2. Surfaces finished by: (a) regular diamond bur, (b) finishing diamond bur, (c) discs and (d) 12 fluted carbide bur.

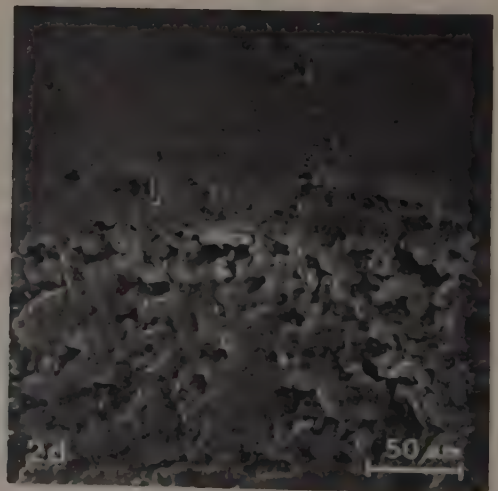
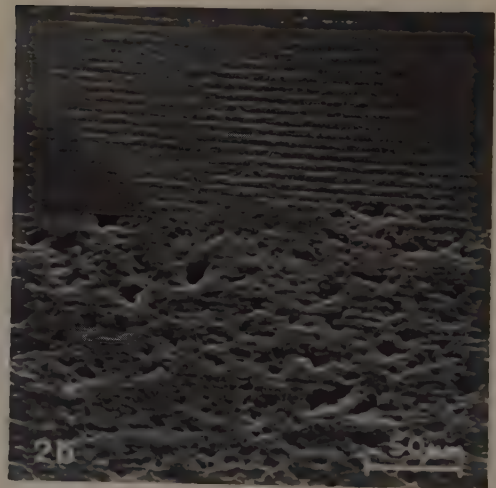
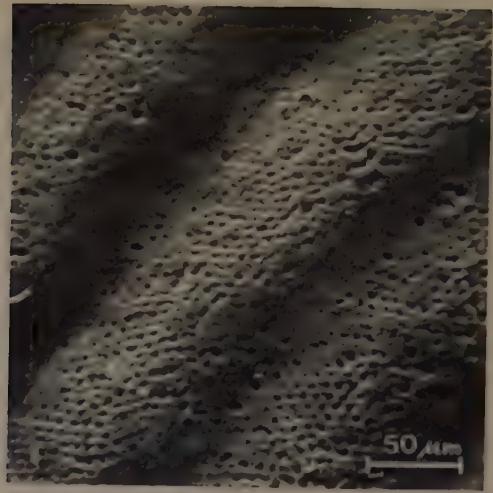
Fig 3. Buccal surface of Class IV restoration (after 20 mo, SGN 1.4 g/cm³) showing smooth areas and areas with a fine surface texture.

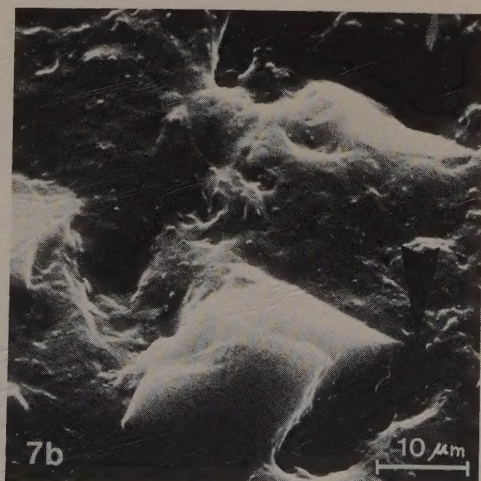
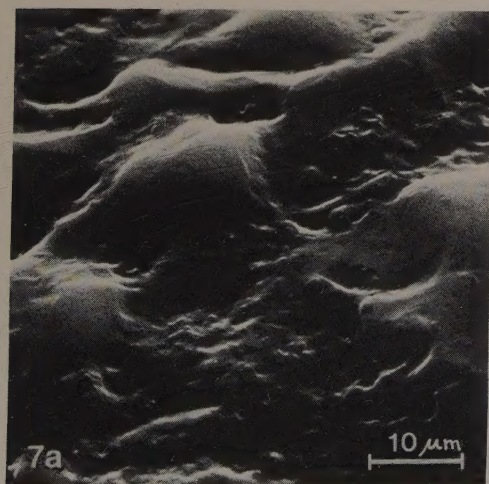
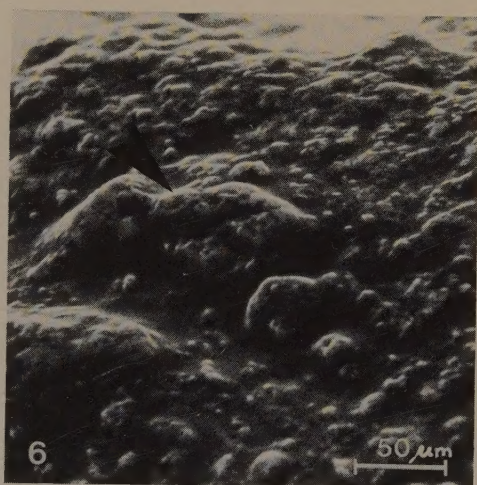
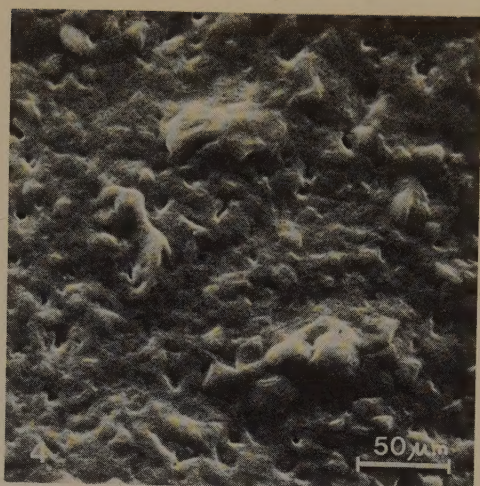
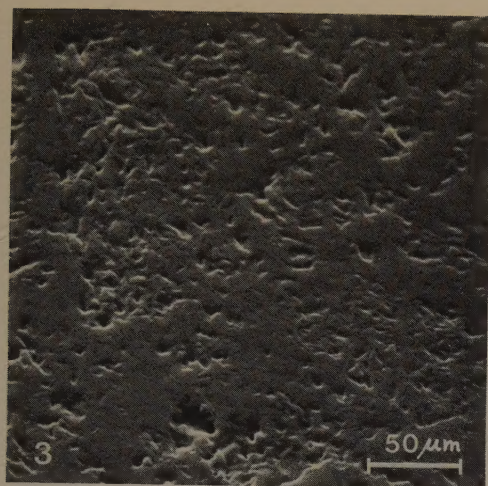
Fig 4. Occlusal surface of Class II restoration (after 12 mo, SGN 1.4 g/cm³) showing fine irregularities.

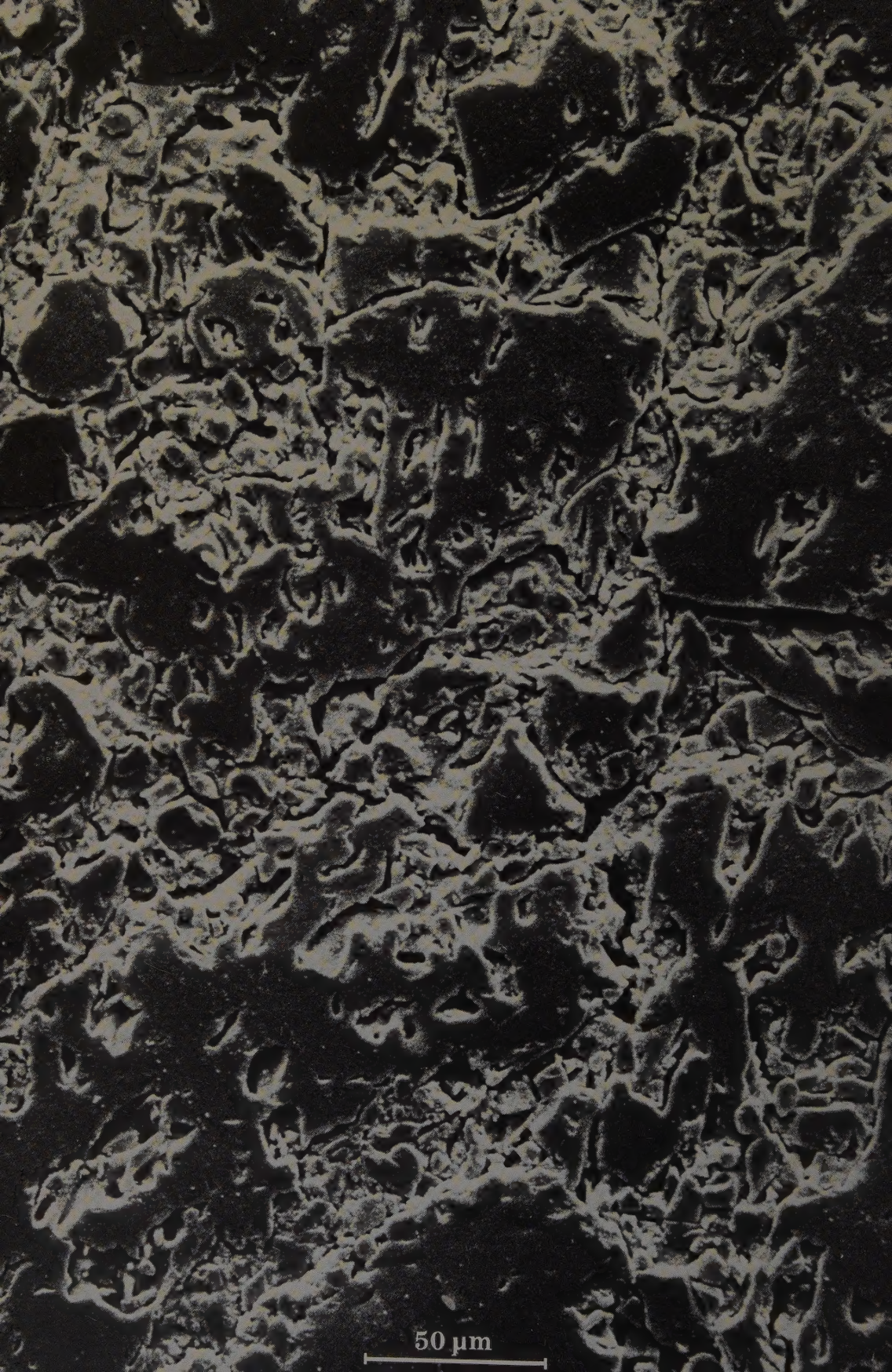
Fig 5. Occlusal surface of a Class II restoration (after 24 mo, SGN 1.0 g/cm³) showing partly exposed particle surrounded by a crevice (arrow).

Fig 6. Part of marginal ridge area of a Class II restoration (after 7 mo, SGN 1.5 g/cm³) showing the rounded-off surface microstructure of an SGN particle containing a small solid sintered area (arrow) and an area (upper right) where the density of the network appears high and the surface fairly smooth.

Fig 7. Surface details from Class I restorations (29 mo) placed in the same premolar. Experimental composite (a) with glass exposed in the surface of a filler particle. Control (b) shows single filler particles with sharp angles and gap (arrow) possibly due to filler dislodgement.







50 μm